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# ELECTRONIC PHENOMENA AT THE SURFACE OF METALS.*

BY

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THE passage of electrons into or out of the surface of metals results in a number of apparently quite distinct phenomena which are studied by very different experimental methods. Among such phenomena one recalls at once photo-electricity, thermionics, contact electromotive force, the reflection and penetration of incident electrons, and the removal of electrons by electric fields or by positive or negative bombardment. Each of these several lines of research has its own interest and importance, but together they have the added interest that one may expect that their correlation will ultimately lead us to a detailed picture of the structure of the surface of metals, which structure, being perhaps only a few molecules thick, is beyond the reach even of X-ray analysis. This problem of correlation is, however, an extremely difficult one, and I have on another occasion discussed some of the discrepancies which appear when one attempts it. For the present, I wish to confine attention largely to three of the above-mentioned fields, namely, contact electromotive force, photo-electricity, and elec-

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tronic bombardment, and in these again to deal more particularly with some results recently obtained by various workers in the Physical Laboratory of the University of Wisconsin. Lest your expectations be unduly raised, I shall say at once that these results do not as yet serve to clear away the discrepancies just mentioned. Nevertheless, I believe they do bring out certain points which are worth consideration.

It has been emphasized many times in the past, that one of the chief difficulties in the field we are considering is the variability of the condition of the surface under examination. This led Millikan, for example, to make photo-electric and contact e.m.f. measurements almost simultaneously on the same surface, which had been prepared by scraping in high vacuum. It has been held, and this view is probably correct, that the variability is due largely to changes in the gas content of the metal surface. What I shall have to say to-day may be summarized as a consideration of the possibility of producing limiting stable conditions of the surface which may perhaps be considered as characteristic of the metal freed from gas, and with the influence of another factor which has been but little discussed, namely, the structure of the metal itself.

Before passing to more detailed considerations it may be well to review briefly the present situation in the fields we are especially considering. The simplest experimental aspect of contact e.m.f. is furnished by the Kelvin method of measurement. If two plates of different metals, say Ni and Cu, are first both connected to earth, and the Ni is then insulated, it will be found that a motion of the Ni with respect to the Cu, changing their relative capacity, will produce a deflection of the electrometer connected to Cu. This may be interpreted as a change in the "bound" charge on Cu, and the e.m.f. which, upon insertion between Ni and the earth, suffices to reduce the deflection to zero, is taken as the measure (with proper regard to sign) of the contact e.m.f. between Ni and Cu. Richardson and Compton were the first to point out that this contact e.m.f. plays a part in photo-electric observations, in the sense that the actual potential difference (tending to retard or accelerate the photo-electrons, as the case may be) between a receiving plate or screen and the plate acted upon by light, should be taken as the difference (with due regard to sign) between the applied potential difference and the contact

e.m.f. Their observations confirmed this hypothesis with rather surprising success, since they were able to combine consistently their own results on the photo-electric effect with previous measurements of contact e.m.f. Thus using a given frequency of light, $\nu$, the photo-electric current is reduced to zero when a certain retarding potential difference is applied (the stopping potential), which satisfies the Einstein equation $V_s - V_c = h(\nu - \nu_0)$. In this equation $\nu_0$ is the low-frequency limit of the metal in question—to wave-lengths longer than this the metal is photo-electrically insensitive. It represents the energy lost by the electron in passing through the surface of the metal, and one might expect it to be identical with Richardson's work function, $\phi$, and related to the contact e.m.f. by the equation $h((\nu_0)_1 - (\nu_0)_2) = (V_c)_{1,2}$ where 1, 2 refer to two different metals, since Page and Millikan have found that with a given receiving plate and a given frequency of light, the actual applied stopping potential $V_s$ is the same for all metals examined. The observed constancy of the stopping potential, $V_s$, implies that an observable proportion (not necessarily all) of the electrons are so situated in the structure of the metal that they have available the full energy quantum $h\nu$, with which to do the work incident to passing out through the surface, that is, overcoming the surface work function. In general, it is not possible to combine consistently the results of contact e.m.f. and photo-electric measurements, nor are the thermionic values of the work function in very satisfactory agreement with the values predicted from the other two types of measurement. A further complication has recently been injected by the very interesting work of Shenstone, who finds that the photo-electric properties of a surface are altered in a semi-permanent way by the passage of an electric current through the metal.

In attempts to age, or in the usual terminology, to outgas, metal surfaces, three processes have been used: Scraping, condensation from another evaporating surface, and prolonged heating in a high vacuum. We have avoided the first named, because it merely serves to expose sub-surface metal whose gas condition is not definite, and have used primarily prolonged heating, combined with distillation for special purposes which will later appear.

Turning now to the experimental results, let us consider first the work on contact e.m.f. which has been carried out by Doctor Dowling, and which has been recently published in detail in the

*Physical Review.* Wax joints were entirely avoided in this apparatus, the Pyrex tube being connected to the pump by a ground glass joint sealed externally with Wood's metal. Each of the metal plates being studied (Cu and Ni) could be separately heated by high-frequency induction, and in such position that the chance of distillation of one metal onto the other was a minimum. Vacuum conditions were such that at the end of the baking-out period (at from 450 to 500° C.) the pressure indicated by the McLeod gauge ($10^{-5}$ mm. Hg = 2 mm.) was only a few millionths of a mm. of Hg, while the separate outgassing of the plates was continued until with the plates hot the gauge indicated no observable pressure. The results must be very briefly summarized and their bearing indicated. First, even after baking out, heating either the Cu or Ni plate to a higher temperature for a few seconds only, by induction, produced very large changes (as much as 1.5 volts) in the contact e.m.f. between them, the plate heated becoming more electro-negative. The Ni plate showed definite indications of reaching a limiting condition, unchanged by either an increase in the time or temperature of heating, but the copper was still changing at the end of ten hours' heating at 1000° C. The shift toward the electro-negative characteristics produced by heating is consistent with the shift of the photo-electric long wave limit toward the ultra-violet, previously observed for other metals; but the form of the curve for both Cu and Ni, namely, falling to a minimum (electro-negative) and then rising toward the electro-positive side again, is not immediately consistent with Hallwachs' and Sende and Simon's curves of photo-electric sensitivity, which first rise to a *maximum* sensitivity and then fall to very low values. Hallwachs proposed a hypothesis of two gas layers, one adsorbed on the surface, the other absorbed into the surface metal layers, to account for his observations, the former being more easily removable. In order to account for the present results the rôle of these layers must be reversed, the adsorbed layer being assumed to render a metal surface more electro-positive. It is probable that the variations in contact e.m.f. with continued heating is due to outgassing, combined with a possible change in structure at present inseparable from it. Surface crystallization was observed at certain temperatures, with the copper, but it cannot as yet be connected with contact e.m.f. changes, probably because the crystals covered only

part of the copper plate. The Shenstone effect undoubtedly plays only a small part in the changes observed with continued heating with a constant current. The situation is evidently very complicated, and apparatus is being designed in which it is hoped to work on several metals at once, measuring both contact e.m.f. and photo-electric characteristics.

The second part of this work was the search for a change in contact e.m.f. due to the structural change from solid to liquid. For this purpose, low melting-point metals, tin and Wood's alloy, were used. It was found that the contact e.m.f. varied a great deal with temperature, the ascending and descending curves being different, a permanent change being produced by heating, which is very likely an outgassing effect, but may be associated with changes in structure. No change as large as .005 volt could be detected at the melting-point, but the solid and liquid phases were different as regards the variation of contact e.m.f. with temperature. The constancy of contact e.m.f. through the melting-point is in agreement with a qualitative prediction of Bridgman, but is at variance with the conclusions of Goetz, who, from observations of the thermionic properties of Cu, Fe and Mn (published since Doctor Dowling's work was begun), concludes that there is a very marked change in the work function of these metals at the melting-point and at other points where crystalline changes were to be expected. It may be that our low melting-point metals were never sufficiently outgassed to allow the effects of structural change to be detected, but the curves do not particularly suggest this. It is evident that much more systematic study of the metals is needed.

Parallel with the efforts to produce stable and limiting conditions of metal surfaces as regards their contact e.m.f. have been numerous studies of their photo-electric properties with the same general object in view. The view of Hallwachs and Sende and Simon that by prolonged heating platinum could be rendered completely insensitive, and their conclusion that probably in general photo-electric sensitivity is only a property of gas-filled surfaces has been pretty definitely shown to be in error. The apparent loss of sensitivity is due to a shift of the long wave limit toward the ultra-violet, beyond the range of wave-lengths available with their apparatus. Hence the values ordinarily given

for the long wave limits cannot be considered as characteristic of the metals themselves, and must be redetermined. For obvious reasons, platinum has received the major share of attention in attempts to locate a definite long wave limit for the gas-free metal. Results obtained at the University of Chicago by Tucker and others, working under Doctor Swann, seem to show definitely that it is possible by prolonged heating in vacuum to push the limit for platinum beyond the range of wave-lengths furnished by the quartz-mercury arc. Our contribution to this question is largely the work of Doctor Welo and Mr. DuBridge, and has been carried out with several forms of apparatus. Provision was made for the use of the hydrogen spectrum after the limit has been pushed beyond the range of the mercury arc. Unfortunately, for our plans, we have not been able, even by prolonged heating in the very highest vacuum, to render the platinum insensitive to the mercury spectrum and so have not been able to use our additional facilities. This is not a peculiarity of a particular form of apparatus, for we have had the same experience with several different forms. The suggestion that our mercury arc is cleaner than the one used at the University of Chicago and therefore transmits farther into the ultra-violet is one I hesitate to make, but since our results place the long wave limit for the best outgassed platinum below 2000 Å., slight differences in the transparency of the quartz would have great influence on the apparent limit.[1] This is not the place for the discussion of detailed differences of procedure, however, and my reason for bringing up the subject at all is to suggest that the possibility that this and other photo-electric uncertainties may be due to the fact that there are two types of surface change produced by heat treatment. The possibility of such a situation is strongly suggested by the last group of results

[1] Since this paper was read we have, at the suggestion of Doctor Langmuir, tried the effect of surrounding our photo-electric tubes with liquid air during the final stages of outgassing the metal, and during observation. While this reduced the time required to reach the final condition, the limiting characteristics were very little changed. We cannot, of course, be sure that these final characteristics are those of the metal freed from gas. There are indications that we may be dealing with an equilibrium gas content of the surface which depends upon the surrounding gas pressure and the temperature of the metal. We are attempting to throw some light on this by the use of vacuum conditions still better than those which have been mentioned above.

which I shall bring to your attention, namely, those obtained by Doctor Farnsworth in studying the bombardment of metal surfaces by low-velocity electrons. Two forms of apparatus have been used. The first was designed primarily for measuring the incident or *primary* electron current and comparing it with the *secondary* current, or those electrons leaving the surface as a result of bombardment. Of course, it is impossible to distinguish, among these secondary electrons, between those which are reflected primary electrons and those which are knocked out of the metal by the impinging primary stream, but it is obvious that when the secondary current is greater than the primary, some secondary electrons must be of the second type. Furthermore, the *velocity-distribution* curve of the secondary electrons, to determine which the second type of apparatus was especially designed, is of such a form that certain inferences as to what is going on may be drawn with some degree of assurance. It has been a satisfaction to find that *both* forms of apparatus may be used for measuring the number of secondary electrons and for determining their velocity distribution and give results in substantial agreement.

With the apparatus just mentioned some ten metals have so far been examined in detail, and out of this material certain general characteristics appear. In the first place, if we plot the ratio of the number of secondary electrons to the number of primary electrons which produce them, as a function of the velocity of the primary electrons, a curve is obtained which it is convenient to call the secondary electron curve, and which turns out to be much the same for all metals which have been outgassed by baking at about 400° to 500° C.

It is a relatively simple curve, showing, primarily, a rapid and then more gradual increase in the percentage of secondary electrons with increasing primary velocity. However, if the metal being examined, or "target" is heated to still higher temperatures in a very high vacuum ($10^{-7}$ mm. Hg or less) the various metals quickly differentiate themselves, and it has been found possible to obtain quite definite limiting curves which are substantially unaltered, by heating either for a longer time or at a higher temperature. The definiteness of these curves, however, is more in their form than in the actual value of their ordinates, and (perhaps for this reason) it seems to be much easier to reach a

fairly stable and characteristic condition of a metal surface as regards its behavior toward bombarding electrons, than in respect to either its photo-electric properties or contact e.m.f. The secondary *velocity-distribution curves* for the thoroughly heat-treated metals show some interesting features, the most important being that, as the primary velocity changes from 15 to 20 volts, there is a definite change in the velocity distribution, in the sense that while for low primary velocities most of the secondary electrons have nearly the same velocity as the primary ones, for the higher primary velocities, on the other hand, an increasing number of slow-moving secondaries make their appearance, and only a small percentage have velocities about the same as the primary. While it is impossible to determine with very great accuracy the primary velocity at which this change takes place, it is without doubt different for different metals, and agrees fairly well in each case with that velocity at which the percentage of secondary electrons increases suddenly. The marked appearance of low-velocity secondary electrons, after this point is passed, strongly indicates that up to this stage the primary electrons are reflected elastically, while for higher velocities they penetrate the surface and either lose most of their energy before turning back or else give rise to an entirely new phenomenon, the emission of low-speed electrons from the surface itself. Following up this point of view, it would be natural to find the noticeable changes in slope of the secondary electron curves associated with changes in the velocity-distribution curve. Especially in the case of copper one is led to explain the well-marked maxima on the basis of a series of inelastic collisions occurring at several definite primary velocities, each resulting in the loss of a certain amount of energy by the primary electrons. If this were the actual process, one would expect that the velocity-distribution curve would show the presence of groups of reflected primary electrons which had *lost* energy corresponding to the velocity at which each type of inelastic impact occurs. But in general, the velocity-distribution curves are more variable and difficult to reproduce than the secondary electron curves and they do not show the simple characteristics just suggested, so that we are led to a different picture of the process. The indications are that as the critical velocities are passed new types of collision occur, but that in each case the primary electrons lose practically

all their energy, and the secondary electrons produced have low velocity.

In general, as the ageing of the target at high temperatures proceeds, the secondary electron curves are lowered, that is, the percentage of secondary electrons is diminished. An interesting question arises as to whether the lowering of the values and development of characteristics peculiar to each metal is due only to the removal of gas from the surface, or whether a change in the structure of the surface, that is, the arrangement of the metal atoms in the surface, also plays an observable part. In attempting to settle this point we have devoted particular attention to copper, whose secondary electron curve is the most individual of all those so far studied. There are three lines of argument, the first of which depends on the result of depositing, by evaporation from another plate and condensation upon the target, a considerable film of copper upon a carefully aged surface which had reached its limiting condition. We find that while an aged and outgassed copper surface gives a secondary electron curve having a number of characteristic maxima and minima, these maxima and minima are almost entirely absent from the curve determined with the condensed layer of copper. The characteristic features will again appear, however, if the condensed layer is given a certain heat treatment. In estimating the significance of this evidence it should be borne in mind that the copper plate from which the layer was obtained by evaporation had itself been thoroughly outgassed before the condensed layer was put down, and that the heat treatment which *restored* the characteristic surface condition was adjusted so that it seemed very certain that the deposited film would not be reëvaporated during the treatment. The interpretation of these results which seems to us most reasonable is that some at least of the characteristics of the aged copper surface are due to its particular structure, these being lost when an amorphous film is deposited upon it, to be again restored when the amorphous film is crystallized or changed by proper heat treatment. The second argument is based on the fact that the exposure of a thoroughly aged copper surface to air at atmospheric pressure resulted in a general increase in the secondary current, opposite to the effect of outgassing, but left the maxima and minima substantially

unaltered. The third but less definite indication is furnished by the result of ageing at progressively higher temperatures and then again at a lower temperature. A consistent interpretation of these results is that the surface structure responsible for the characteristic maxima and minima is most marked when the metal is aged at certain intermediate temperatures and tends to disappear at higher temperature. This idea is supported by observations on copper made incidentally by Doctor Dowling and referred to in the early part of this paper, and also in an indirect way by observations reported by Desch at the Toronto meeting of the British Association. Desch finds that small single crystals of gold (he apparently has not worked with copper) lose more or less completely their surface crystal characteristics (*i.e.*, a sort of surface tension effect comes in) if heated above a certain temperature which is considerably below the melting-point. The same process might well be expected to go on with the surface crystals of our copper plates. Our secondary electron curves for gold are much simpler in form than those for copper—perhaps this represents a real difference between them—perhaps it is due to the fact that we have not yet used just the right ageing temperature to bring out the surface crystallization in a marked degree. The gold surfaces did not show visible crystallization, while the copper did.

The general conclusion from all of this is that there are two changes produced by thermal ageing of a surface in a high vacuum: One the outgassing which in itself is quite complex, and the other the development of a surface structure, and that outgassing in general reduces the number of secondary electrons, while crystallization tends to increase the number and to develop characteristic features in the secondary electron curve. With this point of view fairly well established in connection with the phenomena of electronic bombardment, it is obvious that the same two changes are occurring in the heat treatment of surfaces being prepared for photo-electric or contact e.m.f. measurements and it may be that while it has not been possible so far to separate these two effects—outgassing and change of structure—it is their undetermined combination which is responsible for the variable results which have been obtained and for the difficulty of securing reproducible and stable limiting surface conditions. At least, this is a suggestion which may help in clearing up the present confused situation in the other two fields of research.

# LIMITATIONS OF THE THEORETICAL EQUATIONS FOR THE MOBILITIES OF GASEOUS IONS.*

BY

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## INTRODUCTION.

NUMEROUS attempts have been made to derive satisfactory theoretical expressions for the mobilities of gaseous ions. Most of these have been successful in a minor degree only. None of them has been able to reproduce the difference in mobility of positive and negative ions, none of them can, without the aid of secondary assumptions as to the arbitrary factors occurring in ionic diameters, explain the apparent complete independence of the mobility of the ion and its mass, and finally only two theories can more than estimate the absolute values of the mobilities without arbitrary assumptions as to the size of the ion cluster. Certain new facts have now become known which formulate the problem of ionic mobilities a bit more sharply from the experimental point of view. With the aid of these it seems perhaps best to review the question as a whole and to point out why with our present knowledge it seems impossible to derive a satisfactory expression.

## NEW FACTS ABOUT IONS.

Before proceeding to a discussion of the theories, it becomes necessary to give in outline some of the salient newer facts which the ion theories must explain.

(1) *The Effect of the Inertia of the Carrier on the Mobility.*—It was first noted by Rutherford,[1] and later by Franck,[2, 3] that the mobility of ions consisting of positively charged radioactive atoms in gases like air and $H_2$ had mobilities of the same order of magnitude as the ions formed from the gas molecules in these gases. The experiments of Franck are especially significant, for he found that the mobility of aged ions of ThD in air were slightly larger (1.55 cm./sec.) than the mobilities of normal air ions in air (1.4 cm./sec.). The values are, however, not too accurately comparable as they were not measured under the same conditions. The measurements made on ThD were performed

* Communicated by the Author.

using the radio-active properties, so that the presence of the ThD atom in the carrier throughout its path was assured. Lately, Erikson [4, 5] has repeated the measurements on these ions very shortly after formation and found that the mobilities had two values. The newly formed positive ion had a mobility of 4.35 cm./sec. and the older positive ion a value of 1.55 cm./sec. in good agreement with Franck's value. The comparison with air here is sufficiently certain to establish the fact that the radio-active ion has a slightly greater mobility. The high mobility of the newly formed ion Erikson ascribes to a doubly charged ion, which loses one of its charges on ageing. It is also possible that the higher value of the aged ion is ascribable to the fact that these ions travelled part of their path in the measuring field as a doubly charged ion and increased their average mobility in this way. The existence of the doubly charged ion, if correct, is of great significance as regards the discussion of one of the types of theories of the ions to come later. The conclusion to be drawn is that the ion consisting of a massive positive kernel has essentially the same mobility as the ion whose kernel is a much lighter molecule.

Independently Blanc [6] and Wellisch [7] found that ions formed in $CO_2$ or $CH_3I$, by ionizing those molecules, whose mobilities were measured in air, had the same mobilities as the air ions in air. Lately this work has been carefully repeated by Tyndall and Grindley,[8] who measured the mobilities of ions formed in $H_2$, $CO_2$, ether, and chloroform, in air. The mobilities were the same as for air ions in the air within 1 per cent. Erikson has repeated Tyndall and Grindley's work on the newly formed ions in different gases with much the same result. Unless, as Wellisch at one time assumed, the charge wanders from one molecule to another (a fact strongly argued against by results with radio-active ions), this means that the mobility is almost completely independent of the inertia of the ions. Now all ion mobility theories have a mass factor in which the mobility of the ion depends to some extent on its mass. Perhaps the smallest of these factors is one of the type $\sqrt{\frac{M+m}{m}}$, ($M$ is mass of molecules and $m$ that of the ion), where the value changes from 1.41 for a single molecule to 1.00 for an infinitely heavy cluster. Assuming an ion to be a cluster of some four molecules, the difference in mobility due to

such a small factor between a ThD ion in $H_2$ and an $H_2$ ion in $H_2$ would be 1.005 and 1.12, and for air it would be 1.06 and 1.12. These are differences of from 6 to 12 per cent. and should be detectable. For the cases investigated by Tyndall the values to be expected are not quite so great but should be measurable.

Only one assumption can be made to explain these effects and that is that for the heavier ion [10] the forces exerted by the ion on the gas molecules are not so great and hence a sort of compensation between the mass of the ion and the increase in mobility due to decreased forces of attraction must exist. That the compensation should be so complete is naturally very strange. It indicates definitely, however, that any changes in mobility of ions observed cannot be ascribed to changes in inertia of the ion. Recourse must therefore be had to the variation of the only other quantity, that is, the force field of the ion, or the size of the ion cluster resulting from this variation.

(2) *Changes in Mobility of Newly Formed Positive Ions.*—A second set of phenomena which are of supreme importance for an understanding of ionic nature are the remarkable measurements of Erikson [11, 12] on ionic mobilities in gases shortly after the formation of the ion. It has been shown by Loeb,[13] Wellisch,[14] and Bailey [15] that ionization liberates electrons in a gas, and that in some gases (such as air) a finite time is taken for the electron to attach to a molecule. In other gases such as pure $N_2$, He, $H_2$, it never attaches, and in gases like HCl and $Cl_2$ it attaches very rapidly. In all the gases investigated by Erikson, under the conditions obtaining in his measurements (presence of impurities, and high pressures), the process above does not figure. It is possible that his results for ions generated in $H_2$ may be explained by this phenomenon. Accordingly Erikson works on negatively charged molecules to begin with. His observations show that the *mobilities of newly formed positive and negative ions have the same values, in practically all gases studied.* The positive ions, however, change their mobilities after a time interval from .03 to .001 of a second to the value associated with the positive ions that are normally found. These results receive a confirmation from the old measurements of Todd,[32] using an alternating current method. It is further shown that for the negative ion there is only one mobility. *The two positive mobili-*

*ties refer to two distinct ionic forms with apparently no series of intermediate forms existing,* as shown by Erikson's curves.

Erikson explains these results by assuming the negative ion to be a single molecule which has gained an electron, while the positive ion is *at first a monomolecular ion which later attaches another molecule to form a bimolecular ion.* He finds, however, that the mobility is independent of the number of atoms in the ionized molecule, since initially ionized atoms of Ar, molecules of $H_2$ † and molecules of $CO_2$, all have the same mobility in air.

The explanation given by Erikson is the only one that seems logical at present. For the mass factor having been ruled out by the Tyndall [11] and Grindley [8] measurements, the only two factors left that can change the mobility are the size of the ion or the field of force, the two of which are not independent. It seems very improbable that a change in the field of force of a positive ion could alone cause this. For it seems improbable that such a field should change abruptly by a quantum-like step in an interval of time as long as .03 to .001 of a second. That such a time would be required for a molecule to pick up an adequate companion or companions is not surprising from difficulties encountered in explaining such a phenomenon as recombination of ions,[16] or the attachment of electrons (*loc. cit.*) to molecules. For a molecule to attach to an ion to form a union that is at all stable, it must in the neighborhood of an ion lose most of its kinetic energy of motion due to the field, so that it and the ion describe a small, closed orbit about their common centre of gravity. It is probable that this could take a considerable time and that it would depend on the right type of a molecule coming into its sphere of activity. When the ion had captured its companions it would then have a single distinct mobility differing from that in the unattached state.

This picture, however, has a definite consequence. It indicates that the cluster formation takes place in a *minor degree,* only, as this is essential to explain, the absence of intermediate forms. Furthermore, it is the change in diameter of the cluster which affects the mobility. The consequence of this, as we shall

† This does not apply to the case of negative ions formed in $H_2$ and measured in air. The writer has pointed out above, however, that the small discrepancy noted here is due to the fact that the electron may be attaching in the measuring field to form the ion. Such an effect is to be expected if the $H_2$ as generated is pure.

see, is one of the determining factors in our problem of ionic mobility theories.

(3) *Evidence of Clustering from Mobility Measurements in Mixtures.*—Another series of measurements that permits us to assert the presence of clustering in gaseous ions are the systematic quantitative measurements of the writer on the mobilities of ions in mixtures of gases of widely diverse natures such as air and $NH_3$, and air and HCl. Detailed results and a discussion of them are being published elsewhere.[17, 18] The conclusion, however, is definite; that the ion is accompanied by an increased density of molecules and exerts a preference on the constitution of the gas in its immediate neighborhood.

(4) *Difference in Mobilities of Positive and Negative Ions.*—Finally there is one more phenomenon which has never been explained on any ion theory and will remain for some time to come, a phenomenon amenable only to the qualitative type of explanation to be given by the writer. This phenomenon is the difference in mobility of positive and negative ions. The question has been revived in interest through recent experiments of the writer [19] who showed that contrary to existing beliefs the mobility of the positive ion in HCl was greater than that of the negative ion. Furthermore, the light which has been thrown on this problem by Erikson's [11, 12] work also makes the discussion at this juncture of interest.

All theories of ionic mobilities which have endeavored to use a definite law of force between ion and molecule have resorted to the inverse fifth power law of force. The reason for this is that the ion is supposed to act with such a force on the neutral molecules supposed to be bodies of dielectric constant $D$. This law would hold whether $D$ were caused by a polarization of the molecules in the field of the ion or by the orientation of the electrical dipoles present in the molecules by the field of the ion. The constant $D$ used in all the theories has been the dielectric constant of the gas obtainable from any table of constants. Now $D$ as measured on a gas is independent of the sign of the charge on the ion. That is to say, the polarization of the molecule in the field or the orientation of the molecular dipole in the field as measured for gas molecules in bulk is independent of the sign of the charge causing the field, and is dependent only on the field strength. Thus the mobility should be the same for ions of both signs.

Actually positive and negative ions have different mobilities. In gases of low dielectric constant, or where the mobility is relatively great, the negative mobility is greater than the positive mobility. In other gases such as ether and many vapors the mobilities are nearly equal. Finally in HCl the positive ion has a mobility greater than the negative mobility. Furthermore, as Erikson has shown in gases where the negative mobility is greater than the positive mobility, the mobility of the positive ion when newly formed is equal to that of the negative ion. After a lapse of some time (from 0.03 to 0.001 second), the positive ion mobility reaches its final low value. How the mobility changes cannot be determined, as only the statistical value for a large number of ions can be measured. It is obvious that there are, however, two very definite forms of positive ions.

The nature of the difference of the mobility in the case of the two ions as interpreted by theory requires that use be made of an idea pointed out by the writer in 1917.[10] This explanation is applicable to any ion theory that attempts to calculate the forces between the ions and the molecules on the basis of the forces of dielectric attraction. The polarization which causes the dielectric action of the molecules may be regarded as emanating from two causes, as Debye [19] has pointed out. The neutral molecules may be regarded as being dielectric spheres which in the field suffer an electrical separation which is proportional to the field strength. In this case the units making up charges in such a sphere are to be regarded as very minute and sufficiently close together as to make the action over the surface uniform. Furthermore, they may be regarded as completely mobile. The second cause for the dielectric action of molecules lies in the existence in some of the molecules of permanent electrical doublets. These are continually being disoriented in the field due to the heat motions of the molecules. On the average they have, however, a certain component of the moments in the direction of the field and the amount of such polarization produced by a given field must depend on the temperature. The study of the variation of the dielectric constant of gases with temperature has disclosed the fact that both types of action occur, the dielectric constants of some gases being partly due to one cause and partly to the other. Molecules like $H_2$ or air have very little, if any, permanent dipole strength, while gases like HCl and $NH_3$ have a large amount.

Ether [19] has only about 14 per cent. of its dielectric constant at room temperatures attributable to the permanent dipoles existing. The study of these effects refers to conditions measured in a uniform field.

In the case of the forces between molecules and ions the fields acting on the neutral molecules are sufficiently uniform as long as the molecules are several molecular diameters distant from the ion. When, however, the molecule and ion approach within a molecular diameter of each other (a condition which is most important as regards the action of the molecule on the mobility of the ion), this is far from being the case. The intensely divergent field of the ion is very widely different over the surface of the molecule and the discrete electrical structure of the molecule must be taken into account. For further analysis it is simpler to consider first the case of gases such as $H_2$ and air where there are no permanent dipoles present. In such molecules the electrons are distributed in their orbital paths over the surface of the molecules, while the positive charges are concentrated in the centre. When such a molecule approaches within a molecular radius of an ion some of the surface electrons approach within an ionic radius $\gamma_i$ from the central charge on the ion. The positive charge of the molecule is at a distance $\gamma_i + \gamma_m$ from the central charge of the ion where $\gamma_m$ is roughly the radius of the molecule, or at least of such dimensions. The forces at the distance $\gamma_i + \gamma_m$ on the positive constituent are less than the forces on the nearer surface electrons by a factor $\gamma_i^2/(\gamma_i + \gamma_m)^2$. It is of course true that the superficial electronic orbits are warped in the strong field of the ion. This warping will also be the greater on those portions of the molecule lying near the ion than on the other portions. In spite of this the force in all cases will be stronger on the superficial negative portions of the molecule than on the nuclei or positive constituents. In the field of a positive ion on close approach the negative charges will be attracted more strongly than the positive charges will be repelled, and the molecule will be strongly attracted, perhaps strongly enough to be permanently captured. In the field of a negative ion the superficial electrons will be repelled. But in view of the resistance to the warping of the orbits the electrons will still lie nearer the negative charge on the ion than does the positive charge which is attracted by the negative ion. As a result it will be far less attracted by the negative ion than the

same molecule is attracted by the positive ion. Thus on close contact the positive ions will attract the molecules more strongly than the negative ions do. For the molecules relatively distant from the ion the forces will be about equal and the effect of these on the mobility will be about the same. Thus one might conceive of the lowering of the mobility of the ions due to the forces as being of two sorts. The first one is the one depending on the action of the ions on the molecules at a distance. This in general gives the factor dependent on $(D-1)$, which is the factor that determines the order of magnitude of the mobilities. The second type of action lies in the action on the ions that approach so closely that the sign of the charge on the ion has an opportunity to act differently on the two kinds of ions. This difference in the forces naturally leads to differences in the mobility, and if the clustering that occurs is permanent, the extent of the clustering about a negative ion in this type of gas is distinctly less than about the positive ion. The second factor discussed leads to the depression of the mobility of the positive ion to a value $1/1.29$ that of the negative ion in air. This second type of lowering of the mobility due to the forces at close range cannot be determined from the theories which assume that the ordinary law of dielectric forces holds all the way through. The mobility computed by such equations may lie between the values of the mobility for the negative and positive ions, although it is conceivable that the law of force assumed is so very different for close encounters that the effect on the mobilities cannot be predicted at all. At present it is impossible even to estimate the magnitude of such an effect and ion mobility equations will in all probability lack the factor explaining this effect for some time to come.

For gases like HCl the action is essentially different and an ingenious explanation proposed by Mr. Condon, based on the existence of permanent dipoles of widely differing mass, seems to be adequate. The dielectric constant of this gas depends to some extent on the existence of permanent molecular dipoles. Furthermore, the positive unit in this dipole has a mass very much less than the negative unit. Thus the rotations of the dipole consist chiefly in the motions of the light positive H nucleus about the negatively charged Cl ion. In the strong divergent field near a negative ion the orientation of such a dipole will, on the average, be such as to place the positive H atom nearer the ion than the

negative Cl with its group of electrons that are being repelled. Thus it will be strongly attracted, its attraction for the positive pole being greater than for the negative pole. In the field of the positive ion the orientation will be quite the other way. Owing to its greater bulk the negatively charged Cl ion will not be able to come as close to the ion as did the positive end of the dipole. Furthermore, while the negative electrons are being warped in the direction of the positive ion, the action of the positive H atom of the dipole will serve to reduce this action, and the net result will be that the positive ion will attract the molecule less strongly than did the negative ion. The mobility of the negative ion will thus be reduced below that of the positive ion in this gas. Such an action should occur for the halogen acids, $H_2O$ and perhaps $H_2S$.

For other gases, especially those having high dielectric constants and low mobilities, both types of action between charges and molecules will take place. It is unlikely that outside of gases like the halogen acids and perhaps $H_2O$ and $H_2S$, the extreme dipolar action should occur which makes the mobility of the negative ion less than that of the positive ion. In other gases like $C_2H_5Cl$, $NH_3$, and ether the mobilities of the ions of both signs will, due to these opposing actions, take on values which approach each other, the positive ion in general being slightly less mobile than the negative ion. It is accordingly seen that it is possible by an analysis of the mode of action of the forces between the charges on ions and molecules to explain the differences between the mobilities of positive and negative ions in a satisfactorily qualitative manner.

The differences in the mobilities of the positive and negative ions as interpreted by the Erikson experiments would then mean that the positive ion, owing to its greater force, could in due time attach another molecule and thus create an ion cluster. The negative ion and the unclustered positive ion, while exerting different forces at very close range, will have their mobilities largely determined by the forces on more distant molecules where these are nearly equal. It is nevertheless strange that these differences in forces should not show any difference in mobilities in the case of newly formed positive and negative ions. The peculiar differences of these mobilities and the lack of intermediate forms of ions demand a definite quantum-like action in the

forces which one can only explain by a discontinuous phenomenon like clustering.

### THEORIES OF IONIC MOBILITIES.

The theories of ionic mobilities proposed may for convenience be placed in three general classes. The first and most common type are those that consider the ion as a rigid elastic sphere of dimensions larger than those of the surrounding molecules owing to its attractive forces. These do not exert attractive forces on the surrounding molecules and their mobility depends solely on their increased size and mass. As examples of this type of theory the early equation of Langevin [20, 21] and one due to Lenard [21] serve as excellent examples. Langevin's equation reads:

$$K = \frac{.815}{300}\frac{e}{M}\frac{\lambda}{\bar{c}}\sqrt{\frac{M+m}{m}}, \text{ cm./sec. per volt/cm.}$$

where $\lambda = \frac{1}{\pi\sigma^2 N}$, $N$ being the number of molecules per cm.$^3$, $\sigma$ the sum of the ionic and molecular radii, $e$ the electron, $M$ the mass of the gas molecules, $\bar{c}$ their velocity of thermal agitation, and $m$ the mass of the ion. The equation of Lenard ‡ as a first approximation may be written as

$$K = \frac{.92}{300}\frac{e}{M}\frac{\lambda}{\bar{c}}\left\{\frac{M+2m}{2\sqrt{m(M+m)}}\right\}, \text{ cm./sec. per volt/cm.}$$

where the quantities have the same significance as in Langevin's equation. These two equations, while fairly rigorous, require an arbitrary assumption as to the value of $\lambda$ or $\sigma$ in order that they may be evaluated. This is done in the case of Langevin [22] by assuming that there is a force acting due to the dielectric polarization of the molecules given by $F = \frac{(D-1)e^2}{2\pi N r^5}$, where $D$ is the dielectric constant of the gas, and $r$ the distance of ion and molecule. This law of force is the only one which we can apply in such a case with our present knowledge, and is used in most other theories. It is, however, deficient in certain respects, as was shown in the discussion of the mobilities of ions of different sign. This law leads Langevin to formulate a condition of stability of the ion in which the potential energy, at a distance which gives the stable grouping, must equal the kinetic energy of agitation. From this condition the value of $r$ for a stable ion can be computed and

‡ This is an approximation to a more rigorous form deduced by Lenard later, but for our purposes it is sufficient.

one has a value for $\sigma$. The values of $K$ so estimated do not agree especially well with theory. Furthermore, the factor for the mass in these equations does not make $K$ completely independent of the mass of the ion as the recent experiments of Tyndall and Grindley seem to indicate must be the case. The mobility is furthermore not nearly as independent of the temperature as theory demands. For if, as experiment shows, $K$ is independent of the mass, then unless $\sigma$ varies in such a way with the temperature that as $\bar{c}$ decreases $\sigma$ increases, $K$ will increase as $T$ decreases, the reverse of what Erikson,[30] Phillips,[28] and Kovarick [29] observed.

A second type of theory which was proposed independently by Langevin [20] and Loeb [23, 24] *regards the entire action of the ion as being due to its charge.* All energy exchanges are due to the reactions of ion and molecule under an inverse fifth power law of attraction, the force constant being the same dielectric factor used by Langevin [22] to estimate the size of his ion cluster. The equation of Langevin was deduced as a special case of a more general theory which assumed both these forces to act and elastic impacts involving $\sigma$ to take place. When the factor depending on the size of the ion takes on its limiting form as $\sigma$ becomes insignificant in its action the equation, except for a numerical factor, takes on exactly the same form as the equation deduced by the writer. The writer's equation was deduced by substituting for $\lambda$ in the Langevin equation for elastic impacts above, the value for the mean free path which was shortened by the field of force and was solely due to this as computed by J. J. Thomson.[16] The dropping out of any factor depending on the size of the ion from this expression for the free path followed from an assumption of Thomson's that any impact between an ion and a molecule in which a parameter $p$ is less than $\sqrt[4]{\frac{2(D-1)e^2}{2\pi NMV^2}}$ "there will be no apsidal distances; the bodies will come together and collide." He then postulates that "if the collisions are like direct collisions of elastic spheres, the relative velocity will be reversed by the collision and the colliding bodies will retrace their paths."

With these assumptions (which in view of Langevin's rigorous treatment do not appear to be completely justified), as long as the sum of the radii of ion and molecule at impact are less than the parameter $p$, one can completely ignore the size of the ion

and whether it is a cluster or not. This at once causes the ion to be acted on by a retarding force due solely to its charge, and in which the radius of the ion plays no rôle. It is not surprising then that the equation of the writer as well as that of Langevin should take on the interesting forms:

$$K = \frac{0.104\sqrt{\frac{M+m}{m}}}{\frac{\rho}{\rho_0}\sqrt{(D-1)M_0}} \text{ cm./sec. per volt/cm.}$$

and

$$K = \frac{1.68 \times 10^{-3}\sqrt{\frac{M+m}{m}}}{\frac{\rho}{\rho_0}\sqrt{(D-1)\rho_0}} \text{ cm./sec. per volt/cm.}$$

where $\rho_0$ is the density of the gas at n.t.p. and $\rho$ is the density under any conditions. It is seen that the mobility is independent of the charge. The proof of this would of course establish the correctness of these assumptions, but up to the present there are no certain data available. If the mobilities of Erikson's new ThD ions are due to doubly charged molecules, the evidence is of course strongly negative. The mobilities are independent of temperature and of the size of the ion. They give a mobility proportional to $\frac{1}{\sqrt{(D-1)M_0}}$ in fair accord with facts. The value of $K$ computed from them is of the correct order of magnitude, for the ions with no arbitrary assumption as to size of the cluster. The mobility, however, is not independent of the mass but changes by a factor from 1 to the $\sqrt{2}$, from the case of an infinitely massive ion to one of molecular size. This is in direct contradiction to the experiments of Tyndall and Grindley. Also the theory does not permit of a difference in positive and negative mobilities unless the force factor mentioned before is known. Inasmuch as the experiments of Tyndall and Grindley do not let $K$ vary with the mass of the ion, the experiments of Erikson which show the definite existence of two positive ions, an aged one and a newly formed one, can only be explained by the assumption that $K$ depends in a small measure on the size of the ion. This definitely negatives the use of equations which completely neglect the diameter. The error inherent in it, to wit, that the size of the ion is of no consequence, can be due to one of two causes. First,

in case the actual sum of the radii of ion and molecule are greater than the $p$ assumed by J. J. Thomson, the use of this equation would be wrong. For an ion assuming the forces used in this equation calculation shows that $p$ would be 3.65, 5.02, 6.12 and 9.2 multiplied by $10^{-8}$ cm., respectively, for the gases He, $H_2$, $N_2$ and HCl. If the ion consisted of a layer one molecule deep about the charged molecule, the ionic diameter would be 4.36, 4.94, 7.0 and 4.0 times $10^{-8}$ cm., respectively, for these gases using the kinetic theory values for the molecular diameters. Thus, if clustering took place to any extent, the condition assumed in deducing the theory would not be fulfilled. In the second place, it is very questionable if the assumptions made by Thomson are correct, in which case the molecular diameters would have to be regarded. Thus, interesting as these theories may be because of their simplicity and freedom from assumptions, they cannot be useful except as first degree approximations.

The third class of theories are those in which both the elastic impacts due to rigid portions of the ions, and attractive forces on the outside molecules are taken account of. These theories are probably the closest to reality. For while it is likely that a considerable portion of the impacts could be accounted for on the basis of the orbits described as a result of the laws of force, circumstances must arise as shown by the Erikson results, where the repulsions between the force fields varying very rapidly with the distance, which occur at the so-called "molecular" surfaces and define them, take place. Theories of this sort are numerous. Of the more rigorous ones those of Sutherland,[25] Wellisch,[26] Langevin [20] and Reinganum [27] may be mentioned.

The theory of Sutherland is initially based on his theoretical treatment of the change of the coefficient of viscosity with temperature. He gets an equation for the variation of the mobility with temperature which agrees well with Phillips' [28] results. The latter results are not, however, in accord with similar measurements of Kovarick,[29] and both these disagree with the very accurate measurements of Erikson,[30, 31] made at constant density, which seem to be the most reliable. Using the constants which he derives from the temperature variation, in his mobility equation, and assuming a *small molecular ion,* Sutherland gets values of the mobility 9.6 times as great as those observed. Thus an arbitrary assumption as to increased forces of ions on

molecules must be included which makes the theory rather arbitrary, an electrical friction of 8.6 times the kinetic friction being postulated to make the results agree. The mass variation of mobility is small although not negligible. With the arbitrary factor, a variation in this factor for positive and negative ions in each gas would give the observed mobility differences in positive and negative ions. The same could also be done by varying the radius of the ion in conformity with the results of Erikson, but the equation would cease to be a small ion theory.

The theory of Wellisch [26] is perhaps more interesting. He assumes a small monomolecular ion, and assumes that the elastic impacts of kinetic theory occur. He then calculates the increase in the number of impacts (or, better, the apparent increase of the kinetic theory sum of ionic and molecular radii) produced by the forces acting. He assumes an inverse fifth power law of attraction with a force given by

$$F = \frac{(D-1)\,e^2}{2\pi N r^5}$$

and calculates the apparent increase in the sum of the radii of ion and molecule due to the increased impacts resulting from this law of force. He, in doing this, neglects a factor included in the Thomson [16] treatment of the last section, which is also included in Langevin's [20] treatment. That is, all energy exchanges which do not lead to impact are ignored in Wellisch's theory. These energy exchanges with molecules serve to reduce the mobility of the ion also, and should strictly not be omitted. The derivation of Thomson shows the magnitude of the error introduced by this omission to be about 10 per cent. This is not serious and could be corrected for. In the notation of this paper the equation of Wellisch substitutes for the $\sigma^2$ of Langevin's equation for ions suffering purely elastic impacts, the quantity

$$\sigma^2 \left\{1 + \frac{(D-1)\,e^2}{4\pi N \sigma^4 M \bar{c}^2}\right\}$$

The quantity $\frac{(D-1)e^2}{4\pi N\sigma^4 M\bar{c}^2}$ being nothing but the ratio of potential energy of the molecule at a distance $\sigma$ from the ion, to the kinetic energy of agitation. If this be done the mobility is given by

$$K = \frac{.815}{300}\,\frac{e}{M}\,\frac{\lambda}{\bar{c}}\,\frac{\sqrt{\frac{M+m}{m}}}{\left\{1 + \frac{(D-1)\,e^2}{4\pi N\sigma^4 M\bar{c}^2}\right\}} \text{ cm./sec. per volt/cm.}$$

Taking the equation which Wellisch himself gives, and putting it into the present notation, the equation becomes

$$K' = \frac{e}{300M\bar{c}} \frac{\sqrt{\frac{M}{m}}}{\pi N\sigma^2\left\{1 + \frac{(D-1)e^2}{4\pi N\sigma^4 M\bar{c}^2}\right\}\sqrt{\frac{M+m}{M}}}$$

or

$$K' = \frac{1}{300}\frac{e}{M}\frac{\lambda}{\bar{c}} \frac{\sqrt{\frac{M^2}{m(M+m)}}}{\left\{1 + \frac{(D-1)e^2}{4\pi N\sigma^4 M\bar{c}^2}\right\}} \text{ cm./sec. per volt/cm.}$$

The difference between this equation and the one above lies in the derivation of the expression for the mobility into which Wellisch's expression for the shortening of the free path was introduced.

Wellisch introduces the term for the shortening of the free path into the equation $K = \frac{e}{m}\frac{\lambda'}{\bar{c}'}$, where $m$ is the mass of the ion and $\bar{c}'$ is its velocity. This expression is the simple one deduced, taking into account the distribution of free paths. It does, however, not take into account momentum and energy exchanges between ion and molecule, for it assumes that any energy gained in the field is wiped out at each encounter. This might be the case for monomolecular ions of the same mass as the molecules. The $\lambda'$ which Wellisch uses is the one from classical kinetic theory containing the shortening of the free path by the mass factor as well as the shortening due to the apparent increase in $\sigma$. The combination of this factor with the equation is erroneous for it neglects the fact that although the free path is shortened by increasing the mass of the carrier, the more massive carrier persists in its motion in the direction of the field in collision with lighter molecules. The Langevin equation used above by the writer takes this into account and is the dynamically correct one for inserting Wellisch's expression for the apparent increase in $\sigma$. The Wellisch expression accordingly is more a function of the mass of the ion than the form given by the writer. Both expressions are less a function of the temperature than the simple elastic impact theory. The quantity $\frac{(D-1)e^2}{4\pi N M\bar{c}^2\sigma^4}$, if one use as $\sigma$ the diameter of a molecule (that is, assume a small ion, as

Wellisch does), has in air a value of about 4. This makes the factor an important one and the mobilities yielded by it are of the magnitude observed experimentally. The large value for this factor contains in it, however, a contradiction of the small ion assumption, for it has the potential energy $\frac{(D-1)e^2}{8\pi N\sigma^4}$, greater than $\frac{1}{2}M\bar{c}^2$, the kinetic energy. This means that molecules must be "captured" by the ion and that a cluster forms. If the equation be admittedly a cluster equation, then it is satisfactory as far as it goes, the arbitrary value of the size of the cluster now being required. Erikson claims to have calculated values for the mobilities of his two positive ions (assuming a monomolecular and bimolecular ion), and obtained the observed ratio of the mobilities by its aid. This theory without further assumptions as to the law of force cannot explain the difference between positive and negative ion mobilities.

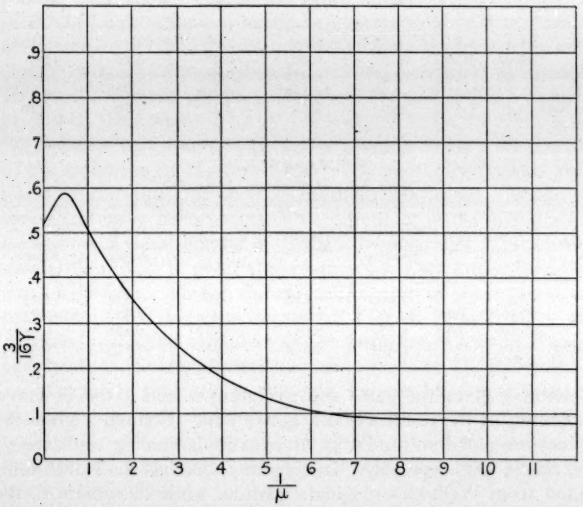
Finally there are the theories of Langevin [20] and Reinganum.[27] They are as rigorous mathematically as the strict kinetic theory and the complexity of the accurate treatment will allow. The theory of Reinganum is different from that of Langevin in that the former replaces a function given by Langevin in the form of a curve by an empirical equation. In our present notation the equation of Langevin reads:

$$K = \frac{3}{16\gamma}\frac{\sqrt{\frac{M+m}{m}}}{\frac{\rho}{\rho_0}\sqrt{(D_0-1)\rho_0}} \cdot \frac{1}{300} \text{ cm./sec. per volt/cm.}$$

Here $\gamma$ is a complex function of $\mu = \sqrt{\frac{3(D-1)e^2}{8\pi N\sigma^4 M\bar{c}^2}}$, which is given by the graph in Fig. 1, where $\frac{3}{16\gamma}$ is plotted against $\frac{1}{\mu}$. $\rho$ is the density of the gas while $\rho_0$ is its density at n.t.p. It is seen that this is the same equation as the one disregarding elastic impacts of rigid spheres given by Langevin above, if for very large values of $\mu$, $\frac{3}{16\gamma}$ reaches the limiting value 0.505. The full equation, if $\mu$ falls in the proper region, should be able to explain most peculiarities of ionic mobilities. It is thus better than the expression of the writer. It has a certain amount of arbitrariness in the value of $\sigma$ chosen, and thus in the value of $\mu$ used. It is,

however, deficient in the respect that all theories are deficient, to wit, that it must rely on the force as given by $\frac{(D-1)e^2}{2\pi Nr^5}$, which must certainly be departed from to a considerable extent at close encounters where clustering is involved. Reinganum has expressed the equation for $K$ in a convenient form, the equivalent factor for $\gamma$ which comes from a graph in the case of Langevin's equation

FIG. 1.




now being expressed in the form of an equation. This equation reads:

$$\frac{3}{16\gamma} = \frac{3\mu}{4\left(1 + 1.486\mu \times 10^{-\frac{0.5253}{\mu}}\right)}$$

in the notation here used. In how far this is an improvement of Langevin's equation is doubtful.

*Values of the Mobilities.*—For the sake of comparison the values of the mobilities in cm./sec. per volt/cm. for two types of ions have been computed on several of the theories discussed, for four typical gases and for the case of an ion made up of a $H_2$

molecule moving in the four gases, by Mr. A. M. Cravath. The two types of ions are single molecular ions and ions consisting of a monomolecular layer of twelve molecules grouped about one central molecule.§ The values are given in Tables 1 and 2 below.

TABLE I.

*Monomolecular Ions.*

| Gas. | Observed + Ions | Observed − Ions | Langevin Elastic Impacts. | Original Wellisch. | Corrected Wellisch. | Loeb Forces Alone Acting. | Complete Langevin Forces and Elastic Impacts. |
|---|---|---|---|---|---|---|---|
| Air.... | 1.4 | 1.8 | 9.85 | 1.28 | 2.08 | 1.12 | 3.17 |
| $H_2$.... | 6.02 | 7.68 | 67.5 | 6.08 | 9.90 | 6.21 | 17.3 |
| HCl... | .65 | .56 | 4.47 | 0.356 | 0.58 | 0.382 | 1.06 |
| Ether.. | .19 | .22 | 2.56 | 0.181 | 0.294 | 0.208 | 0.565 |
| $H_2$ ions in air | 1.4 | 1.8 | 35.9 | 5.53 | 4.82 | 3.09 | 8.70 |

TABLE II.

*Cluster Ions of Eighteen Molecules.*

| Gas. | Observed + Ions | Observed − Ions | Langevin Elastic Impacts. | Original Wellisch. | Corrected Wellisch. | Loeb Forces Alone Acting. | Complete Langevin Forces and Elastic Impacts. |
|---|---|---|---|---|---|---|---|
| Air.... | 1.4 | 1.8 | 1.80 | 0.128 | 1.46 | 0.822 | 1.63 |
| $H_2$.... | 6.02 | 7.68 | 12.3 | 0.795 | 9.08 | 4.60 | 10.23 |
| HCl... | .65 | .56 | 0.817 | 0.051 | 0.582 | 0.280 | 0.657 |
| Ether.. | .19 | .22 | 0.468 | 0.028 | 0.318 | 0.153 | 0.363 |

Column 1 gives the gases used, columns 2 and 3 the observed mobilities of the positive and negative ions. Column 4 gives the values computed on the Langevin equation assuming collisions of the elastic solid type only. In column 5, one has the values computed from Wellisch's original equation, while in column 6, the values computed from the corrected form of Wellisch's equation given by the writer are included. Column 7 gives the mobilities computed on the writer's theory, which assumes all impacts as being due to the force fields and neglects elastic impacts. In the last column the results of Langevin's complete theory are given.

It is of interest to observe that the elastic impact theory of

§ A layer of twelve molecules was chosen as this is the maximum number of spheres that can be grouped around a sphere of the same radius. Prof. A. Joffé, of Leningrad, who was kind enough to read the manuscript, points out that from considerations based on crystal structure a layer of six molecules would have been more nearly correct. The results serve, however, to give an idea of the magnitudes involved.

Langevin requires a cluster to give mobilities of the right order of magnitude, although even then they are a bit high. The clustering assumption makes the original Wellisch equation, which agrees fairly well for a monomolecular ion, fail completely, although it was shown that the law of force assumed makes clustering probable. This is due to the mass factor mentioned before. The Wellisch theory as modified by the writer changes little in value where clustering occurs. The values are perhaps slightly better for the cluster ion. The writer's own theory also is nearly independent of clustering and would be entirely so were it not for the mass factor. Finally, the complete Langevin theory agrees more closely with experiment when the cluster formation is assumed. Its values are not as good as either the corrected Wellisch equation or that of the writer.

Another very interesting fact is brought to light in the case of the mobilities of $H_2$ ions in air. The mass factor makes these much greater than the ionized air molecules in air. While the theoretical mass factors cause little difference in the mobilities of ions of the same or greater mass than the molecules in which they move, they cause a great difference when they are lighter than those molecules. This in the case of $H_2$ ions in air is completely contradicted by the experiments of Tyndall and Grindley and Erikson. That this should be so for the negative ions in $H_2$ is to be expected, for the electrons cannot attach to $H_2$ molecules to form negative ions and so negative ions in $H_2$ are not ionized $H_2$ molecules, but molecules of impurity. In the case of the positive ion the complete failure of the predicted mobility can indicate but one thing, and that is a cluster formation with heavier molecules.

## SUMMARY.

One may summarize the foregoing in the following fashion. The remarkable degree of independence of the mobility and inertia of the ion forces one to ascribe the ageing effects found by Erikson to changes in diameter of the ion. For such quantum-like but slowly reached changes in ionic force fields are not in conformity with our knowledge of the molecules. The changes in diameter, however, must be small. Further evidence for clustering in ions comes from the recent work of the writer in mixtures of gases. An attempt is next made to explain the differences in positive and negative ion mobilities by a study of

the structure of the molecule in a qualitative fashion. This leads to the conclusion that further quantitative progress in an understanding of ionic behavior requires that the law of force between molecules and ions at close approach be known. This means that little progress can be made in this direction for some time to come.

A review of ionic mobility theories shows that the only ones which are capable of explaining the results in the light of this evidence are those which consider elastic impacts between ions and molecules which exert forces on each other. The best of these is doubtless the one due to Langevin, as computations based on it which are beyond the scope of this article show. It in turn is defective in the same sense that all theories at present must be defective in that it has not the true law of force between ions and molecules at close approach. Until such a law can be found further theoretical work is futile. The values of the mobilities can be computed within the accuracy permitted by the lack of more adequate knowledge of the forces by the modified theory of Wellisch, that of the writer or the more accurate theory of Langevin.

In conclusion the writer wishes to express his gratitude to Messrs. Cravath and Condon, two of his students, the discussion with whom has been very useful in clarifying his ideas.

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**The New Pharmacopœia.**—The Pharmacopœia of the United States of America, Tenth Decennial Revision (U.S.P., X) became official on January 1, 1926. This treatise is the tenth revision of the original Pharmacopœia which was adopted by the Pharmacopœial Convention of 1820, and published by its authority in that year. The president of this convention was the distinguished scientist, physician, and statesman, Samuel L. Mitchill.

Since 1820, the Pharmacopœia has been revised every ten years by a Pharmacopœial Convention, the Tenth Revision being issued by authority of the convention of 1920. The Pharmacopœial Convention was incorporated in the District of Columbia in 1900. Meetings are held every ten years in the City of Washington; the delegates represent certain branches of the Federal Government, incorporated colleges of medicine and of pharmacy, the national medical, pharmaceutical, and chemical societies, incorporated state medical and pharmaceutical societies, and certain organizations which were represented in the convention of 1900.

The Pharmacopœia of 1820 was a treatise of 272 pages; the text was bi-lingual on 206 pages; the descriptions of the drugs and directions for their preparation were given in both English and Latin. Rubrics of purity, methods of assay, and synthetic organic compounds were omitted, or else unknown.

The Pharmacopœia of 1920 (the Tenth Revision), which is a book of 688 pages, is written entirely in English, with the exception of the Latin names of the drugs. The monographs on vegetable and animal drugs, chemicals, and preparations cover 417 pages. Tests are given for the identification of the various drugs, and for the determination of their purity, maximum values being set for impurities. Assays are described for the quantitative analysis of certain

drugs, usually to determine the amount of active constituent present. Physiological or biological assays are described for preparations of aconite, digitalis, strophantus, ergot, epinephrine (adrenaline), pituitary, and cannabis, and for cod-liver oil; these assays are of value when chemical analysis does not measure the potency of therapeutic action of a given preparation.

During the past century, a host of synthetic organic compounds have been incorporated into the Pharmacopœia. Among those included in the Tenth Revision are: Acetanilid, acetylsalicylic acid, barbital, the chloramines, cinchophen, epinephrine, saccharine, methenamine, phenolphthalein, procaine, salol, sodium cacodylate, thyroxin, and phenolsulphonephthalein. Chemotherapy has contributed chaulmoogra oil and ethyl chaulmoograte, which are remedies for leprosy; arsphenamine and neoarsphenamine, the treponemocides or specifics for diseases produced by animal parasites of the genus *Treponema* and related species; and by emetine which exerts a specific destructive action upon amœba. Physical chemistry is responsible for the silver protein compounds and for the modified Dakin solution, while immuno-chemistry is represented by the antitoxins for tetanus and diphtheria.

Almost two hundred drugs, which were official in the Ninth Revision, have been omitted from the new edition. Forty drugs have been added to the Pharmacopœia in the Tenth Revision; among them may be mentioned brandy, whisky, barium sulphate, chaulmoogra oil, dextrose, and numerous synthetic organic compounds. The names of forty-six pharmacopœial drugs have been changed in the new edition; several examples may be given. Benzosulphinide (saccharin) is now designated as gluside, calcium oxide as lime, copper sulphate as cupric sulphate, hexamethylenamine as methenamine, hydrated chloral as chloral hydrate, lead oxide as lead monoxide, phenylcinchoninic acid as cinchophen, spirit of nitrous ether as spirit of ethyl nitrite, sugar as sucrose, sugar of milk as lactose, vaccine virus as smallpox vaccine.

The term "cubic centimetre" has been restored, replacing the term "mil" which was used in the Ninth Revision. This cubic centimetre is the millilitre.

To each article in the text is appended a list of the preparations in which it is an active essential ingredient.

The Pharmacopœia has gained in importance during the last two decades, for it is the legal standard for all drugs included in its text, according to the terms of the Federal Food and Drugs Act of 1906, and the drug acts of the various states including Pennsylvania.

The original Pharmacopœia of 1820 was published at Boston, the Sixth Revision (1880) was published at New York; all other revisions, including the Tenth, have been published at Philadelphia.

J. S. H.

# A METHOD FOR GENERATING AND MEASURING VERY WEAK RADIO-FREQUENCY CURRENTS.*

BY

**WALTER van B. ROBERTS.**

Engineer, Radio Corporation of America.

A SOURCE of radio-frequency currents of extremely small but fairly accurately known magnitude is sometimes desirable. For example, in measuring the over-all radio-frequency voltage amplification of a radio set an obvious method of procedure would be to measure the voltage that must be applied to the grid of the detector tube in order to produce a certain output, and then to measure the voltage that must be applied in the antenna circuit in order to produce the same output. But the radio-frequency amplification as defined by the ratio of these two voltages will often exceed 100,000, and as only a tenth or a hundredth of a volt would usually be applied to the detector, it is necessary to have available a source of known voltage of the order of magnitude of one microvolt or less.

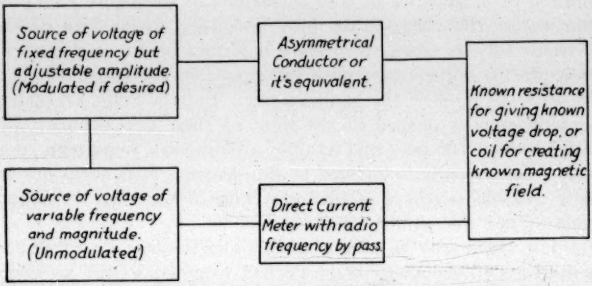
The usual way to obtain weak radio-frequency currents or voltages is to generate enough current to measure with an alternating current meter, and then attenuate it as much as desired. It is not easy, however, to shield the large generated currents and voltages so perfectly that their direct effect upon the radio set will be small compared with that due to the output of the attenuation box, especially if very great attenuation is used. And, furthermore, the action of the attenuation box should be carefully calibrated as it is likely to behave differently toward currents of different frequencies, and not at all as calculated unless designed with great care.

The subject of this paper is a scheme whereby no attenuation at all is required. The current having the desired frequency is generated only in the amount that is actually used, so that the radio set can receive no other voltage of the desired frequency than that due to the known current flowing through a known resistance to produce a known voltage, or flowing through a coil to produce a known magnetic field. An equally important feature of the method is the fact that the radio-frequency current is

* Presented at a meeting held Thursday, December 10, 1925.

measured by a direct current meter so that there is no difficulty in measuring currents of the order of one microampere or less. The method is based upon the well-known fact that when two simple harmonic voltages are impressed in series upon a circuit containing an asymmetric conductor or its equivalent, the resulting current contains in general components of the following frequencies: Zero, twice each of the impressed frequencies, the sum of the impressed frequencies, and their difference. Under certain conditions (see note 1) a very simple relation exists

FIG. 1.

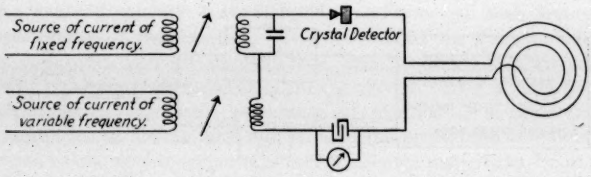

Source of voltage of fixed frequency but adjustable amplitude. (Modulated if desired)
Asymmetrical Conductor or it's equivalent.
Known resistance for giving known voltage drop, or coil for creating known magnetic field.
Source of voltage of variable frequency and magnitude. (Unmodulated)
Direct Current Meter with radio frequency by pass

between the magnitude of the zero frequency or direct current component and the amplitude of the current of the difference frequency, which will be referred to as the "beat" frequency. Under such conditions the amplitude of the beat-frequency current may be accurately inferred from the reading of the direct current meter. It is convenient to keep one of the applied frequencies constant and vary the other in order to generate various beat frequencies. I have found 3000 kilocycles to be satisfactory for the fixed frequency as a small percentage range of frequencies for the other oscillator will then produce a relatively large percentage range of available beat frequencies in the neighborhood of 1000 kilocycles. Modulation may be applied to the fixed frequency source and the beat-frequency current will be found to be modulated to the same degree, and furthermore this degree will remain identically the same, no matter what beat frequency is being generated. (See note 2.)

Fig. 1 shows the method diagrammatically. Fig. 2 shows a very simple arrangement for carrying out the idea. Fig. 3 shows

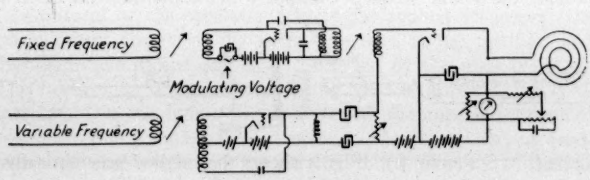
a more elaborate arrangement built to minimize the reactions of the variable couplings upon the oscillator frequencies. A tuned circuit is used in connection with the fixed-frequency oscillator in both Figs. 2 and 3 so as to eliminate harmonics which, beating with harmonics of the variable frequency oscillator, produce numerous frequencies lying in the desired range. These unwanted beats are further reduced by running the variable frequency oscil-

FIG. 2.




lator with as little plate coupling as possible so as to generate a minimum of harmonics. Modulation is effected in the radio-frequency amplifier rather than in the oscillator in order that the degree of modulation may be set to any desired value by plotting the amplifying power of the tube as a function of grid potential and then applying whatever audio-frequency voltage input may be necessary to give the required degree of modulation. The

FIG. 3.

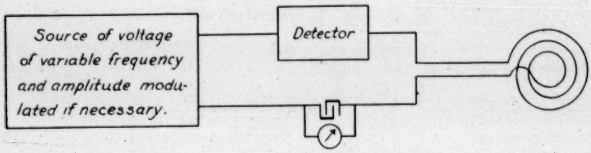



amplifier tube is used as a peak voltmeter to determine the audio-frequency input. When a tube is used as a detector its normal plate current is shunted around the meter by a suitable potentiometer device, and the readings corrected to take account of this device is parallel with the meter. (The correction is negligible if the resistance of the shunt is large compared with that of the meter.)

The general method described above gave excellent results

where extremely weak currents were the goal. By calibrating the couplers it was possible to reduce the current to about a thousandth of the minimum that could be read directly on the microammeter, without likelihood of serious error. As one microampere could be read directly with ease, this means that the output current was known fairly accurately down to about a thousandth of a microampere. With the tube used, however (a U.V. 201-A), the maximum output that was obtained, without

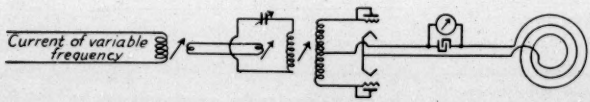
FIG. 4.




noticeable violation of the condition mentioned in note 1 for simple square law response, was only about fifteen microamperes.

A variation from the beat method was next tried with the idea of getting greater output current and reducing the complication of building and operating. Instead of using two frequencies, a single one was applied and the approximate equality between the resulting direct current and double-frequency current was relied upon to justify the use of the direct current meter to measure the double-frequency output which constitutes the desired

FIG. 5.



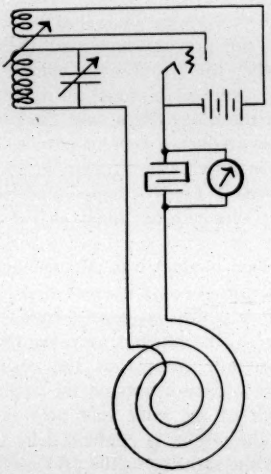

current. (See note 3.) Fig. 4 shows the method schematically. In this method, however, there is some danger of direct pick-up of second harmonic from the oscillator, which should be minimized by making the oscillator coils astatic, or by shielding them, or both, and by keeping the receiving set a few feet from the oscillator. Furthermore, if voltage due to the second harmonic of the oscillator is impressed upon a simple detector, it will send double-frequency current through the output circuit unmeasured by the meter. Hence it is necessary to add means to avoid this. Two ways of avoiding this are shown in Fig. 5. A tuned link

circuit greatly reduces the proportion of second harmonic voltage applied to the detector, and the use of two detectors in a balanced circuit balances off most of the residual second harmonic current, leaving as the only output current of double frequency, that which is generated in the detecting system and hence measured by the direct current meter. This arrangement was capable of giving several milliamperes output of direct current, but a calibration would be necessary to find out the exact relation between this and the double-frequency current under conditions of such heavy overloading of the detectors. This system has the disadvantage as compared with the previous one that the tuned link circuit must be retuned when the frequency is altered. Also, it does not assure strictly the same percentage of modulation at different frequencies as did the first system, and the percentage of modulation of the double-frequency current is twice that of the fundamental. The last mentioned fact (see note 4) is not a disadvantage however, as it is easily compensated for by modulating the oscillator only one-half as much as the degree desired in the output current.

The last described method was not developed to the point it seemed to merit because one of its very disadvantages suggested still a third variation which has proved much simpler and about equally satisfactory. This consists of using the previously undesirable second harmonic current as the desired current. The fundamental of the oscillator acts as the applied frequency, the grid-filament circuit of the same tube acts as the rectifier, and the magnitude of the output is controlled by the plate coupling. The functioning is the same as in the previous method, but is all carried out in one tube. Fig. 6 shows all the apparatus required for generation of unmodulated current. As the tickler, or feedback coil, is brought up toward the tuned circuit, oscillations commence gradually, giving as little as one microampere of rectified current at first. By increasing the coupling the rectified current may be raised to a milliampere if a filament of considerable emission is used. A slight disadvantage is that varying the coupling varies the frequency quite noticeably. In this system, as in the preceding one, the percentage of modulation is doubled and there is no assurance of the percentage of modulation staying constant as frequency or amplitude is varied. If modulation is desired it can be effected by any of the well-known means except

grid modulation. The simplest is to insert the modulating voltage in series with the plate battery. The Heising system, or constant current system, is applicable but requires another tube. Like the preceding system again, this system requires a calibration if accurate values of the double-frequency current are to be inferred from the meter reading when the output is large. The coils in this system are preferably astatic, and a moving coil type of feed-

FIG. 6.



back adjustment is shown, but any type of feed-back control should do as well.

The test for proper operation of this system, as of all the others, is to replace the field producing coil by a short-circuiting link and see that the residual effect is negligible.

As a result of working with the three schemes outlined above, it was concluded that for the production of the very smallest currents the first system is complex but otherwise ideal, while the last system, due to its extreme simplicity, should be valuable in portable field strength measuring sets, where modulation is not required.

NOTE 1.

Let the current through an asymmetric conductor be represented by a power series of the applied voltage

$$i = A + Be + Ce^2 + De^3 + Ee^4 + Fe^5 + \cdots \quad (1)$$

Now let the applied voltage be $a \cos pt + b \cos qt$ and assume that the total circuit impedance is substantially the same for all frequencies dealt with. If a tube detector is used this means that the coil in the plate circuit used to produce magnetic field must have a reactance that is small compared with the internal resistance of the tube. If this is not the case, a further complication is introduced into the calculation, but as the assumption is easily satisfied, the more general investigation need not be included here.

Substitute $a \cos pt + b \cos qt$ for $e$ in equation (1) and reduce the result to a series of simple harmonic terms by tedious but straightforward trigonometry. As a result of terms up to and including the fifth, there will be found direct current of the value $\frac{1}{2}C\,(a^2 + b^2) + \frac{3}{8}E(a^4 + 4a^2b^2 + b^4)$ while the amplitude of current of frequency $\frac{p-q}{2\pi}$ is $C\ ab + \frac{3}{2}E\ ab\ (b^2 + a^2)$.

If $E$ is zero, it is obvious that the total direct current is the sum of the direct currents that would be produced by voltages $a \cos pt$ and $b \cos qt$ acting separately. If $E$ is not zero this would not be true, as one term depends upon the product $a^2b^2$. Hence if we keep the values of $a$ and $b$ so low that the direct current produced by their simultaneous application is the sum of the direct currents produced by them acting separately, we know that the term in $E$ is negligible. And if the $E$ term is neglected, then the amplitude of current of frequency $\frac{p-q}{2\pi}$ is equal to twice the square root of the product of the direct currents produced by the two applied voltages acting individually. We thus obtain the following working rules:

(1) To test whether the meter gives a correct value of the beat-frequency output, short-circuit both oscillators and adjust the meter to zero. Then allow one oscillator to oscillate and observe the meter reading. Now stop this oscillator and start the other and note the reading. Finally let both oscillators go at once, and if the meter reading is equal to the sum of the two previously obtained readings, the detector is acting as if it obeyed a simple square law as far as we are concerned.

(2) To measure the radio-frequency output, observe the readings due to each oscillator separately as in (1); the beat-frequency amplitude will be twice the square root of the product of the two readings.

NOTE 2.

In note 1 it was shown that the rectifier operated as a simple square law device over the legitimate range of inputs. Now if one of the inputs be modulated (taking modulation by a single frequency as illustrative), we have for voltage input $a \cos pt + b(1 + m \cos rt) \cos qt$, where $m$ gives the degree of modulation, which is 100 per cent. if $m = 1$.

Substituting in the squared term of equation (1) (note 1), we obtain a number of new frequencies, but the only term of frequency near $\frac{p-q}{2\pi}$ is the term proportional to $ab(1 + m \cos rt) \cos (p-q)t$ which represents the beat-frequency current modulated in exactly the same way as was the original input at frequency $\frac{q}{2\pi}$.

NOTE 3.

If an asymmetric conductor is used whose current may be represented by the power series of equation 1 (note 1) and a voltage $e \cos pt$ is applied, consider the effect of the $n^{\text{th}}$ power term.

$$\cos^n pt = \left(\frac{1}{2}\right)^n 2 \left\{\cos npt + \frac{n}{1} \cos (n-2)pt + \frac{n(n-1)}{1 \cdot 2} \cos (n-4)pt + \cdots\right\}$$

Where the last term is of zero frequency (and of amplitude equal to one-half the value of the coefficient in $n$) if $n$ is even, as it must be to contribute either direct current or double frequency. The coefficient of the next to last term (the double frequency) is easily found, from the way the series runs, to be

$$\frac{n(n-1)\cdots\left(\frac{n}{2}+2\right)}{\left(\frac{n}{2}-1\right)!}$$

while the last term, or direct current, is

$$\frac{1}{2}\left\{\frac{n(n-1)\cdots\left(\frac{n}{2}+1\right)}{\frac{n}{2}!}\right\}.$$

Whence the ratio of double frequency to direct current $= \frac{2n}{2+n}$.

Thus it appears that the reading of the direct current meter must lie between the correct value of the double-frequency amplitude and one-half the correct value. If $n = 2$, as is the case before the detector is overloaded (from our present point of view), then $\frac{2n}{2+n} = 1$ and the meter reads the double-frequency current correctly.

Instead of supposing that the rectifier is simply asymmetric, consider the case where it is a one-way valve or unilateral conductor. This is approximately the case when a two-electrode tube is used with an adjustment such that with no impressed alternating voltage the current is zero, but will flow in one direction upon the slightest provocation. For small inputs the current may be assumed to vary as the square of the applied voltage. A complete cycle of voltage then produces zero current for half a cycle, and a hump having the shape of a sine wave squared during the other half. This is easily shown by Fourier's analysis to be equivalent to a series of components proportional to $\frac{1}{4} + \frac{4}{3\pi}\sin pt - \frac{1}{4}\cos 2pt - \frac{4}{15\pi}\sin 3x - \frac{4}{105\pi}\sin 5x$, etc., so that the direct current is equal to the amplitude of the double-frequency current.

As the input voltage increases, the current varies more nearly linearly with voltage, so that conditions approach those of the ideal rectifier which is a constant resistance to voltage in one direction, but infinite resistance to voltage in the other direction. A cycle of applied voltage would produce half a cycle of zero current and half a cycle of sine wave. By the same method of analysis this sort of output current may be reduced to the series $1 + \frac{\pi}{2}\sin pt - \frac{2}{3}\cos 2pt - \frac{2}{15}\cos 4pt - \frac{2}{35}\cos 6pt$, etc., showing that the meter reading will be half again as much as the amplitude of the double-frequency current.

From the analysis given in this note for special cases, it can be seen that no exact relation can be given between direct- and double-frequency currents in the output of rectifiers in general, but that there is an approximate equality that will be good enough for many purposes. To find the exact relation for a particular rectifier would require measurements at different inputs, or a knowledge of its volt-ampere characteristic.

NOTE 4.

When a modulated voltage, $a \sin pt(1 + m \sin rt)$, is impressed upon a square law rectifier, the squaring action gives a term in the resulting current proportional to $a^2 \sin^2 pt(1 + m \sin rt)^2$. But $\sin^2 pt$ is equivalent to direct current plus double frequency. So the double-frequency term is proportional to $\sin 2pt(1 + 2m \sin rt + m^2 \sin^2 rt)$. Now if $m$ is small compared with unity, this is very nearly equal to $\sin 2pt(1 + 2m \sin rt)$, or a double-frequency current modulated twice as much as the voltage applied to the rectifier. If $m$ is not less than, say, $\frac{1}{4}$, the term $m^2 \sin^2 rt$ will become apparent, introducing the audio-frequency of modulation $2r$, which was not in the original modulation at all. This is similar to the distortion produced by over-modulation in ordinary radio transmission, and is easily cured by the same process, namely, reducing the degree of modulation.

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**Measurement of Water in Water-power Installations.**—Inasmuch as large water-power plants are usually constructed under a guarantee of a certain amount of power per cubic foot or other standard unit, accurate measurement of such supply is important. Dr. L. A. Ott, of Kempton, Allgäu, contributes to the *Wasserkraft-Jahrbuch* for 1924, a comprehensive paper on the efficiency of the several forms of meters now in use. He points out that, as might be expected, the choice will depend on circumstances. The treatise is in a certain measure an extension of the discussion of the chapter on discharge measurement in the British "Standard Test Code for Hydraulic Power-plants" issued on the occasion of the World's Power Conference in 1924. The copy in hand is a reprint from the above-mentioned Jahrbuch. The paper is illustrated with numerous tables and graphs, and supplemented by a bibliography. H. L.

**A New High-temperature Thermometer.**—The General Electric Company announces the construction of a thermometer capable of measuring temperatures over 1000° C. It consists of a quartz stem and bulb with gallium as the expanding liquid. The metal must be of high purity, otherwise, like mercury, it will stick to the side of the tube. Gallium is a very rare metal, but appreciable amounts of it have been found in lead-containing residues from zinc ores in Oklahoma and Missouri. As no special commercial value has attached to gallium, these residues have been worked for the lead only, but now there will be a strong inducement to extract the rarer metal. In the graduation of the quartz stem special methods had to be used as the ordinary hydrofluoric acid method used for common glass did not answer. (GUY BARTLETT, News Bureau, General Electric Company.)

# CRITICAL IONIZATION POTENTIALS BY POSITIVE-ION IMPACT.*

BY

WILLIAM J. HOOPER, Ph.D.

ABSTRACT.

THE experiments of several previous investigators were repeated in substance with apparatus designed to make it possible to distinguish between ionization and certain spurious factors which have made questionable much of the existing evidence relating to ionization by positive-ion impact. A great many current-potential measurements and curves were obtained at different gas pressures and with a variety of electrical arrangements. The data and curves thus obtained present direct evidence (*a*) that the previously so-called "ionization current" is due to a secondary electron emission from the platinum walls of the ionization chamber, (*b*) that this secondary electron emission is produced by the impact of the positive ions with these metal walls, (*c*) that either there is no ionization in hydrogen gas by the impact of the positive ions accelerated by potential differences up to 925 volts, or that if this phenomenon exists, as is indicated by visual and spectroscopic evidence, its effects are so small at relatively low pressures (.012 mm.) that it is completely masked by secondary phenomena which make its detection by the ordinary direct methods problematic, and (*d*) that it seems possible that at relatively high gas pressures (considerably above .012 mm.), ionization by positive ions might be an important factor with accelerating potential differences between the ends of their M.F.P. well within this same range of voltages.

## INTRODUCTION.

In a recent paper by J. Franck [1] attention is called to the limited and deficient knowledge that exists concerning critical ionization potentials by positive-ion impact. Reference is made to the work of several investigators in this field and a theoretical explanation offered for their seeming inability to obtain a sharply defined minimum ionizing potential in the so-called "current-potential curves." Experimental evidence exists, however, which impugns the interpretation of these curves as being due to ionization of the gas and indicates that they may be the result of a secondary electron emission from the metal parts of the apparatus under positive-ion bombardment. Thus existing evidence seems to be somewhat contradictory. That the minimum energy required by a positively charged particle to dislodge an electron

* Communicated by the Author.

from a gas molecule is approximately the same as that required by an impacting electron seems to be supported by the experiments of E. V. Bahr and J. Franck,[2] Pawlow,[3] Dempster,[4] Townsend,[5] Saxton,[6] and others. In contradistinction to this, however, the experiments of Tate,[7] and Horton and Davies,[8] would indicate that the ionization potential of a gas molecule by positive-ion impact might be considerably higher than that due to impact by an electron. The present work was undertaken with the object of clearing up some of the uncertainties, and endeavoring, if possible, to obtain definite information concerning this subject by eliminating some of the spurious elements which enter work of this nature, such as those due to the photo-electric effect caused by resonance radiation, the liberation of secondary electrons ($\delta$-rays) from the walls of the ionization chamber under positive-ion bombardment, etc. To this end apparatus was designed with the view of eliminating effects due to resonance radiation by employing the Compton method.[9] The manner in which effects due to secondary electrons were distinguished will be illustrated further on in this paper.

## EXPERIMENTAL PROCEDURE.

The ideal attack on this problem would seem at present to be to work with H-nuclei in hydrogen. This was the basis for the recent work of Saxton.[6] However, a study of the apparatus employed by Saxton, from the published article, has lead to the conclusion that the effects interpreted as due to ionization could be equally well explained as due to secondary electrons liberated from the gauze (employed to accelerate the positive ions) under positive-ion bombardment, and drawn to the collecting electrode by the positive retarding field. The work of Horton and Davies,[8] H. Baerwald,[10] and Holst and Osterhuis,[11] appears to afford adequate grounds for this conclusion. The recent work of Smyth,[12] Hogness and Lunn,[13] and also that of Dempster,[4] would indicate that $H_2^+$ and $H_3^+$ ions might have been predominant, instead of $H^+$ (H-nuclei) as assumed by Saxton. The result of Saxton's work, therefore, appears to be very inconclusive. It seems at present experimentally problematic to work with H-nuclei in H over a sufficiently low range of speeds and eliminate the many spurious elements which beset work in this field.

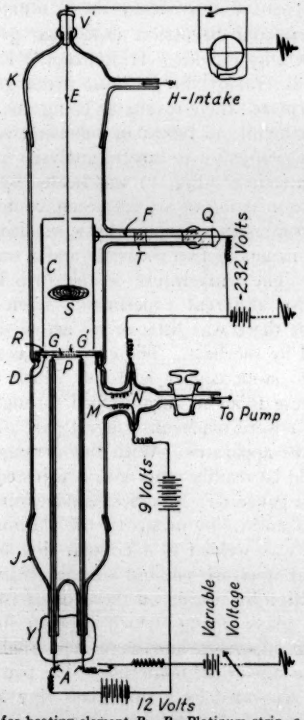
In the present work a heated platinum strip coated with a thin

layer of sodium phosphate, produced by the evaporation of a water solution, furnished the source of positive ions. In some of the experiments the heated platinum strip alone served as a source, the salt having been removed by excessive heating. The exact nature of the positive ions from these sources is unknown, although an interesting discussion as to their probable nature is contained in papers by Pawlow,[3] Hüttemann,[14] Richardson,[15] and Erikson.[20] As several of the previous investigators used these sources and interpreted their results as being due to ionization, it seemed well worthwhile to repeat in substance some of the previous work and to subject it to careful analysis.

The platinum strip $P$ (Fig. 1) was heated by means of three storage batteries consisting of six cells each, connected in parallel. The heating current was measured by a sensitive ammeter and kept constant by means of two rheostats and a small copper slide-wire resistance. The temperature of the strip in these investigations varied for different experiments from about 800° to 1100° C., so that there was little or no actual disintegration of the metal caused by the heat. The current was carried into the apparatus by two stout copper leads $A$, which fitted snugly in glass tubes. These tubes in turn slipped through closely fitting glass tubes which were made an integral part of the removable lower end $J$ of the apparatus. With this arrangement the platinum strip $P$ could be readily removed or adjusted to any desired distance from the gauze $G$. Electrical connection was made with the two gauzes $G$ and $G'$ by means of the platinum leads $M$ and $N$. Each gauze was welded to a circular disc of platinum and covered a circular aperture cut out of the centre. The gauzes were held in position by resting on the ends of two short, snugly fitting pieces of glass tubing, which in turn fitted within the main tube of the apparatus and were supported by three glass dents blown in the side of the main tube. The platinum discs with the gauzes were separated by a thin glass ring 2.25 mm. thick, ground from a piece of glass tubing. A cylinder $C$ made of thin platinum foil .001″ thick and closed at one end, except for a small circular opening at the centre, was supported by a nickled-brass rod $F$, which screwed into a piece of brass riveted to a band of sheet platinum that fitted securely over the upper end of the cylinder. The cylinder was thus kept entirely free from contact with any other part of the apparatus. Platinum wire, .011″ in

diameter, was coiled spirally into a flat circular piece $S$ which hung within the cylinder from a small platinum hook that was tightly imbedded in a stout brass rod held securely by the amber insulator

FIG. 1.




*A*—Copper leads for heating element *P*. *P*—Platinum strip, 2 mm. wide, .001" thick. *R*—Platinum ring support for "extracting" potential gauze. *D*—Platinum ring support for "accelerating" potential gauze. *G* and *G'*—Platinum gauze, .008" diameter, 20 strands per cm. *S*—Platinum wire spiral (collecting electrode). *C*—Platinum foil cylinder, 9 cm. long, 3.7 cm. diameter. *E*—Platinum wire lead (to electrometer or ground). *F*—Nickled-brass rod (to electrometer or ground). *Q*, *T*, and *V*—Amber insulators. *Y*—Sealing wax. *M* and *N*—Platinum leads to *G* and *G'*, respectively.

*V*. The plane of the spiral was parallel with the plane of the gauzes. For clearness of illustration the spiral is shown slightly tilted about a horizontal axis in the figure. Hydrogen was pre-

pared by electrolyzing a water solution of $P_2O_5$ in pure distilled water and was then passed through a fine glass capillary needle valve into two large drying tubes filled with calcium chloride and phosphoric anhydride powder, and thence into the apparatus. The needle valve was controlled electromagnetically, thus making it possible to vary the pressure without difficulty and to permit a fresh stream of hydrogen to circulate throughout the apparatus during the course of the experiments. A mercury condensation pump, together with an auxiliary oil pump, was used to exhaust the apparatus. A mercury trap and a small tube filled with gold leaf prevented mercury vapor from the condensation pump and McLeod gauge, respectively, from entering the ionization tube. When not in use the ionization tube was cut off from the condensation pump by means of a large stopcock placed between the tube and the trap. Ground joints were made where the two end pieces $K$ and $J$ joined the main tube, and sealing wax was used to make these joints air-tight, as well as at the amber insulators $V$ and $Q$, and at $Y$. The platinum parts were boiled in strong nitric acid for several hours and then rinsed with distilled water before being placed in the apparatus. All glass parts were carefully washed with "cleaning solution" and rinsed with distilled water, great care being taken to prevent contamination while assembling. The "baking out *in vacuo*" process was tried during the preliminary work by wrapping the main part of the tube with asbestos and then winding on an electrical heating coil. As much difficulty was encountered by cracking the tube with this method, and inasmuch as a good vacuum was obtainable without it, the baking out process was abandoned.

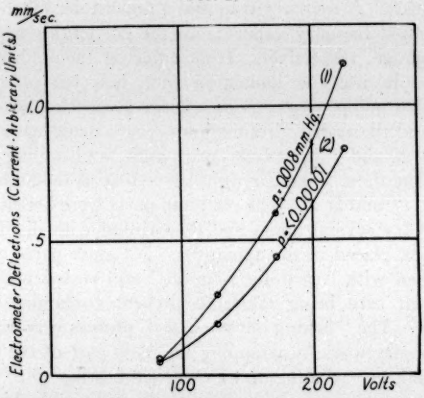
The experiments described in this paper were performed over a considerable range of gas pressures, using a series of different electrical arrangements. These experiments can be classified in the following order:

### 1. REPETITION OF PAWLOW'S WORK.

A repetition in substance of Pawlow's work in this field was made. The electrical arrangement for this experiment is shown in Fig. 1. Positive ions were accelerated into the ionization chamber where they met a strong retarding field which turned them back on their paths or to the walls of the ionization chamber. Electrons liberated within the chamber by ionization or other

processes were drawn by the strong retarding field to the collecting electrode where a quadrant electrometer measured the rate at which the charge accumulated. The curves obtained in this manner were very similar to those obtained by Pawlow, who interpreted them as being due to ionization of the gas molecules by the impacting positive ions. The work of Horton and Davies [8] with positive ions from a glowing tantalum filament in helium has, however, raised a question as to whether this interpretation is

FIG. 2.




correct. The latter investigators came to the conclusion that the effects they observed were due to secondary electrons liberated from the walls of the ionization chamber under the bombardment of the positive ions. To find out whether this was the case or not under the present circumstances a series of further experiments was performed.

With the same arrangement as that just described measurements were taken over a range of accelerating potentials while the pressure was kept constant at .008 mm. The apparatus was then exhausted to a pressure below that measurable by the McLeod gauge and less than $10^{-5}$ mm. Hg. At this low pressure the negative current was again measured over the same range of accelerating potential differences for the positive ions. The results were plotted and gave the two curves shown in Fig. 2.

The proximity of the two curves would indicate that the greater part of the observed phenomena at the higher pressure was not due to ionization of the gas molecules, but rather to secondary electrons liberated from the walls of the ionization chamber by the bombardment of the positive ions. For were the effect due to ionization of the gas, it would have been reduced to an imperceptible value at the very low pressure and curve (2) would not exist. The ionization effect, if any, must therefore be included in the difference between the ordinates of these two curves. As it is possible that even this difference in ordinate values might be due to other causes, it became necessary to study the positive emission from the heated strip. Assuming that both curves are due to secondary electrons from the walls, a difference in the ordinates of the two curves could be accounted for by assuming a difference in positive-ion emission at the two pressures. It is possible that a difference in the positive emission from the heated strip, such that more ions were emitted at the lower pressure, would have raised a curve at the lower pressure and made the secondary electron emission appear more prominent than it really was. If, however, the positive emission decreases with the pressure, it becomes obvious that the difference in ordinates could be due to this cause, and that the values of the lower pressure curve cannot be ascribed to an increase in secondary electron emission relative to ionization. F. Horton [18] has investigated the positive emission in hydrogen from a heated platinum strip coated with sodium phosphate. It is interesting to note from his work that the positive emission from such a source decreases as the gas pressure is lowered. Since in the present experiment the same value for the heating current was maintained at both pressures, the temperature of the strip $P$ would naturally be slightly higher at the lower pressure. The decrease in emission at the lower pressure noted by Professor Horton might possibly be compensated for by the slight increase in temperature of the salt in the present case.

To test the positive emission at the two pressures, the cylinder $C$, gauze $G'$, and spiral $S$ were all connected to the electrometer. Gauze $G$ was grounded and the platinum strip $P$ raised to a positive potential of a few volts. A series of four measurements showed that the emission was approximately the same in the two

cases. An accurate comparison, however, of the intensity of the positive ions emitted from the heated salt at very low and relatively high pressures, was not possible. The result of this investigation leads one to conclude that the curve (2) (Fig. 2) is due entirely to secondary electrons liberated from the walls of the ionization chamber. The difference in the two curves, however, remains to be explained.

At this stage of the work it was necessary, due to experimental difficulty, to replace the platinum strip *P*. In order to investigate further the cause for the difference in the two curves an attempt was now made to compare the measured negative current at the two pressures by adjusting the positive emission to the same value at both pressures. This was found very difficult to do, especially at the very low pressures where the positive emission was very unsteady and often fell off rapidly to such small values as to make the measured negative current almost nil and detectable only when the positive ions were accelerated by a potential of at least a hundred volts or more. This unsteadiness at very low pressures had not been noticed with the first strip of platinum which was somewhat heavier and larger than that employed in the second case. This second strip had been reduced in size to avoid excessive heating about the wax joint *Y*. Several attempts were made to make comparisons of the measured current for the two pressures of approximately .008 and $10^{-5}$ mm. One point only on the curve was selected for comparison in order to keep the time element between measurements as small as possible. The positive emission was measured, by the method previously described, at a pressure of less than $10^{-5}$ mm. The connections were then quickly changed and the negative current measured for the selected value of the accelerating potential of the positive ions. After raising the pressure to a value corresponding to about .008 mm. the positive emission was adjusted until measurements of it corresponded to the same value as obtained at the lower pressure. The connections were then quickly changed to measure the negative current for the same value of the accelerating potential as before. The order in which these measurements were taken was also reversed. As previously stated, the results obtained by this method were not uniform and in some instances the positive emission at the very low pressure fell off so rapidly that measure-

ments of the negative current were useless. However, on one occasion fairly constant measurements were obtained which support very well the proximity of the two curves shown in Fig. 2, obtained with the first strip of platinum. These measurements are shown in Table I, which gives the values for the measured negative current taken consecutively as shown in the third column. The figures show a considerable decrease in intensity with time. This effect was always enhanced by an adjustment of the heating

TABLE I.

| Order in Which Measurements Were Taken. | Positive Emission Current mm./sec. | Negative Current mm./sec. | Pressure mm. Hg. | Heating Current Amps. |
|---|---|---|---|---|
| 1 | 10.65 | | $10^{-5}$ | 4.93 |
| 2 | | 6.58<br>5.81<br>4.81<br>3.33<br>3.33<br>2.86 | $10^{-5}$ | 4.93 |
| 3 | 10.65 | | .009 | 4.95 |
| 4 | | 6.67<br>4.71<br>4.38<br>3.85<br>3.57<br>3.33<br>3.12 | .009 | 4.95 |

current to a new value. Even at constant pressure it was often found very difficult to hold the emission constant. This unsteadiness has been noted by other investigators.[16]

The comparison of the two values of the measured *negative* current in this case, as shown in Table I, shows them to be the same within the limits of experimental error. This would indicate that the negative-current curves shown in Fig. 2 are due entirely to secondary electrons liberated from the platinum walls of the ionization chamber under positive-ion bombardment; the difference of the curves in Fig. 2 being due merely to accidental differences in ion emission at the times when the measurements were made. Thus, though inconclusive by themselves, these experiments at low pressures definitely indicate that the greater part of the measured negative current is not due to ionization of the gas.

### 2. EXPERIMENTS AT DIFFERENT PRESSURES WITH LARGE RETARDING FIELD.

These experiments were in substance the same as those under (1), except that they were performed with a considerable number of different gas pressures. The curves thus obtained indicated the behavior of current-potential measurements for different pressures using a large retarding field. Though interesting in themselves, a very careful study of these curves from the standpoint of possible contributing causes, taking into account mean free path considerations, revealed the fact that it was not practical to extract definite information as to their causes and for this reason the curves are not shown.

### 3. EXPERIMENTS AT DIFFERENT PRESSURES WITH SMALL RETARDING FIELD.

In these investigations the same conditions prevailed as for the experiments under (2) except that now a small retarding field was used. This arrangement permitted most of the positive ions possessing a velocity greater than that produced by 7.5 volts to penetrate the entire length of the ionization chamber. A large family of curves was obtained for accelerating potential differences up to 915 volts, but as in the previous case the behavior of these curves with pressure variation was found to throw no definite light on the problem under consideration and so are not shown.

### 4. EXPERIMENTS IN WHICH AN ATTRACTING FIELD INSTEAD OF A RETARDING FIELD WAS USED, ALSO A COMPARISON OF THE EFFECTS CAUSED BY ATTRACTING AND RETARDING FIELDS.

These investigations were undertaken to study the effects produced when the positive ions were drawn to the collecting electrode by a small attracting field instead of being repelled by a retarding field. This arrangement was of importance because the measured current would now include the *positive*-ion products of ionization, if such existed, instead of the negative electrons.

The capillary needle valve was adjusted to maintain a constant pressure of .012 mm. The mean free path of the positive ions at this pressure was such as to enable most of the ions to acquire the maximum energy obtainable from the applied potential difference between $P$ and $G'$ before colliding with the gas molecules. The positive ions penetrating the entire length of the

ionization chamber should have experienced at last thirteen or more collisions with gas molecules. Measurements were made over a range of accelerating potential differences up to 915 volts, and, as would be expected, the curve, in general, showed a gradually increasing positive slope indicating the presence of a gradually increasing number of positive ions in the ionization chamber. In order to compare this curve with one obtained when a *retarding* field was applied, as described under (3), consecutive observations were made with the two different arrangements at a pressure of .012 mm. The two curves shown in Fig. 3 were obtained in this manner. It is of interest to note that the current to the electrometer is positive in both cases. Curve (1) rises to a positive maximum and then takes a negative slope, showing the rate at which electrons within the ionization chamber decrease the positive charge on the spiral due to incoming positive ions. Curve (2) shows the rate at which positive ions from the platinum strip, and any due to ionization, charge the spiral electrode for the various accelerating potential differences. An explanation for the short negative slope at the beginning of curve (2) might be that electrons were being picked off from the gauze $G'$ by the bombarding positive ions. This explanation is definitely supported by experiments to be described in a later section of this article.

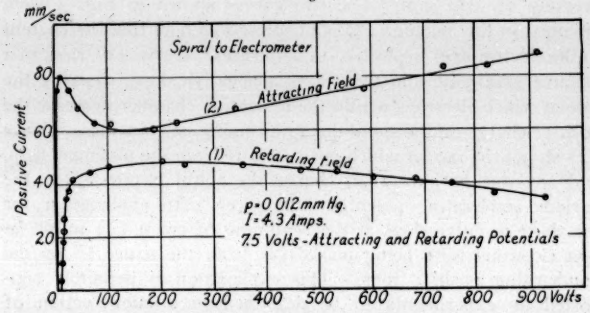
### 5. INTERCHANGE OF ELECTRODES WITH SMALL ATTRACTING AND RETARDING FIELDS.

It now became a matter of great interest to investigate further the source of the electrons within the ionization chamber. It is apparent that if they are due to a secondary electron emission from the cylinder walls, then their intensity should be roughly proportional to the area which is bombarded. Thus, if we connected the cylinder, instead of the spiral, to the electrometer and observed the current (with a small retarding field), we should obtain a much smaller negative current if these electrons were due to a secondary emission from the walls, for in this case only the small area of the spiral would furnish the surface of negative emission, whereas in the case of the spiral to the electrometer the entire inside of the cylinder was exposed to bombardment as a source for the current. On the other hand, if the electrons were the result of a gaseous ionization we would expect that such an

interchange of electrodes (with both a retarding and attracting field) would produce two curves very similar in shape and slope to those shown in Fig. 3.

With the cylinder thus connected to the electrometer in place of the spiral two curves were obtained (Fig. 4) and it was a matter of capital interest to find that curve (1) (Fig. 4) had a positive instead of a negative slope. Had there been no secondary electrons liberated from the walls of the ionization cham-

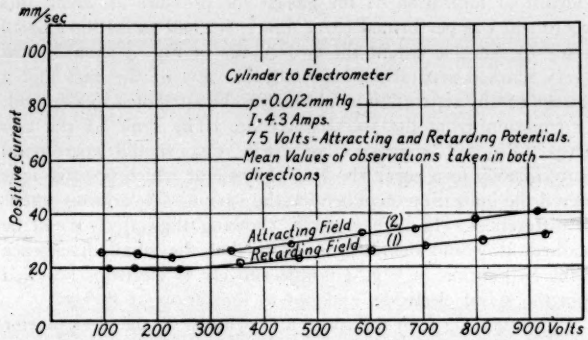
FIG. 3.




ber we should have expected curves (1) (Figs. 3 and 4) to have had approximately the same slope. It is of further interest to note that curves (2) in the same two figures have slopes very nearly identical. This would indicate that the rate at which the positive ions increased within the ionization chamber was the same in the two cases. It would also indicate that there was no appreciable *positive-ion* emission from the metal surfaces under ionic bombardment. The difference in curves (1) is therefore very clearly traced to the difference in the respective areas of the spiral and cylinder exposed to positive-ion bombardment, and the resulting difference in the secondary electron emission from these areas. In order to show clearly the actual difference in the slope of curves (1), the plotted results of two sets of individual readings, taken under the same experimental conditions, are shown in Fig. 5, the ordinate values of curve (2) being adjusted by a constant factor to bring the two curves together for a comparison. These curves give very definite evidence that a secondary electron

emission from the walls constitutes the major part of the observed negative current. Positive support is thus given to the earlier results obtained from the experiments performed at very low pressures. It is to be remarked that, after completing the experiments yet to be described, and just prior to writing this paper, a few measurements similar to those made for the curves shown in Fig. 5 were obtained at a much higher pressure (.10 mm.), and the two curves were found under these circumstances not to

FIG. 4.




have such a marked difference in shape and slope, curve (2) actually becoming negative at the highest values of the accelerating *P.D.*, whereas curve (1) became negative at very low values. At this stage of the work it became impossible to continue the experimental work without completely rebuilding the tube, because of cracking and contamination. These latter observations would indicate one of two things, either that ionization of the gas by positive-ion impact is a phenomenon which becomes prominent only at higher gas pressures, or that the secondary electron emission from the spiral electrode increased considerably with the gas pressure. It is to be mentioned that Professor Townsend [17] states precisely that at higher gas pressures ionization of the gas by positive-ion impact would be an important factor, whereas at lower pressures a secondary electron emission from the cathode might be expected to predominate.

Attention is particularly directed to the marked similarity of

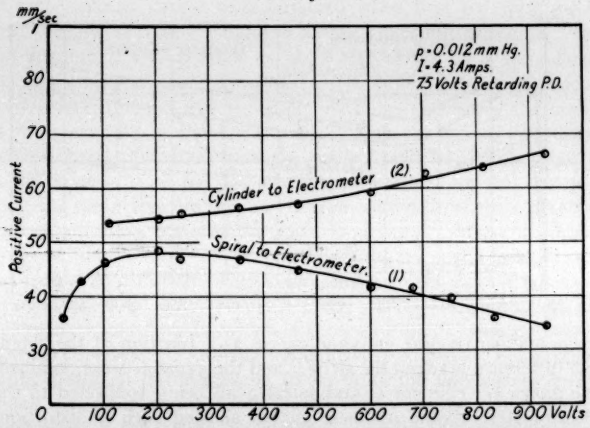
curves (1) and (2) shown in Fig. 4. There is at most only a very small difference in the slope of the two curves. This small difference would be expected, since the positive-ion bombardment of the spiral electrode should produce a small secondary emission, which when drawn to the cylinder by the positive retarding field would make the positive slope of curve (1) less than that of curve (2), also a lesser number of positive ions would strike the cylinder in this case, due to the small retarding field, though this effect would be small. From these results it is obvious that there is no evidence of ionization of the gas at the pressure at which this experiment was performed (.012 mm.), for had ionization existed to any measurable extent the two curves in Fig. 4 should show a very marked separation, especially in view of the fact that a fraction of any separation would have to be attributed to a secondary emission from the spiral electrode. The slope of the two curves (Fig. 4) suggests that curve (2) should correspond approximately to a curve showing the rate at which positive ions entered the ionization chamber for the various accelerating potential differences. If such a curve, showing this effect, could be obtained, it would definitely indicate that the small divergence of the two curves in Fig. 4 is due entirely to electrons knocked from the spiral electrode, and not to ionization of the gas.

By connecting both the spiral and cylinder to the electrometer and grounding the gauze $G'$, the arrangement was such that the desired curve should be obtainable. Since there was no electric field applied within the ionization chamber for these measurements, any secondary electron emission from the metal walls or from ionization of the gas should produce no appreciable effect on the measured positive current. The plotted results of observations taken in this manner revealed a curve which had approximately the same general shape and slope as curve (2) (Fig. 4). This was a very significant observation. In order to confirm this result and the results represented by the shape and slopes of all the curves (Figs. 3, 4 and 5), repeated measurements were taken consecutively, covering the group, using a condenser in the circuit to obtain measurements which would conveniently show all these curves on the same plot. These results are shown in Fig. 6. The points indicated by $X$ and $\Delta$ show the values of the measured current with no applied field within the ionization chamber. Curve (1) was obtained on one afternoon

and the other five curves on the following day. These curves represent average values of measurements made in both directions of ascending and descending potential differences, and their general shape and slope have been confirmed by repeated observations.

An analysis of the curves will now be made. Perhaps the most outstanding point of interest is the fact that curves (4), (2), (6) and (1) all have approximately the same slope. If

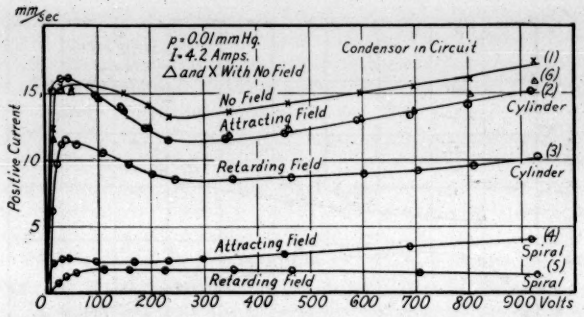
FIG. 5.




ionization of the gas had been present to any measurable degree we would certainly expect curves (4) and (2) to have greater slopes than curves (1) and (6). The fact that they are not greater is direct evidence that ionization of the gas did not exist to any measurable degree with the apparatus and experimental conditions under which these investigations were carried out. The similarity of curves (1) and (6) to curve (2) shows that the predictions regarding the slope of curve (2) (Fig. 4) were fulfilled, definitely indicating that the separation between the two curves (1) and (2) (Fig. 4) and (2) and (3) (Fig. 6) is due to electrons knocked from the spiral. As to the source of the negative electron current in this experiment there seems to be

only one outstanding answer. If this current is due entirely to secondary electrons liberated from the walls of the ionization chamber, then these curves have a very clear and logical explanation. On the other hand, it seems impossible to explain them on the basis of a gaseous ionization produced by the positive ions. This experiment also gives an explanation of the hump at the beginning of some of the curves. There seems to be little question but that this is due to electrons liberated from the gauze $G'$. A

FIG. 6.




large number of pure emission curves as a function of the potential difference between the strip $P$ and the gauze $G$ were obtained, the gauze $G'$, cylinder $C$ and spiral $S$ all being connected to the electrometer. None of these curves showed such a distortion. On first consideration one might think that, due to the relatively large potential gradient between the two gauzes, separated by only 2.25 mm., all the negative electrons liberated from the gauze $G'$ would be drawn to $G$. However, when we consider the strong beam of positive ions bombarding the gauze $G'$ in one direction, it appears very possible that a considerable number of electrons might easily be knocked from the gauze in this same direction and escape from the electric field between the gauzes. This phenomenon has been observed by Dempster [4] for slow canal rays, who found that if the holes in the cathode were relatively large, electrons appeared. It has also been observed by Wien [18] for fast canal rays. The negative slope of this hump from about 25 to 225 volts in curves (2) and (3) might indicate considerable

recombination of the positive ions with the secondary electrons knocked from the gauze $G'$, although Baerwald has shown such a type of recombination to be small.

#### 6. INTERCHANGE OF ELECTRODES WITH STRONG RETARDING FIELD.

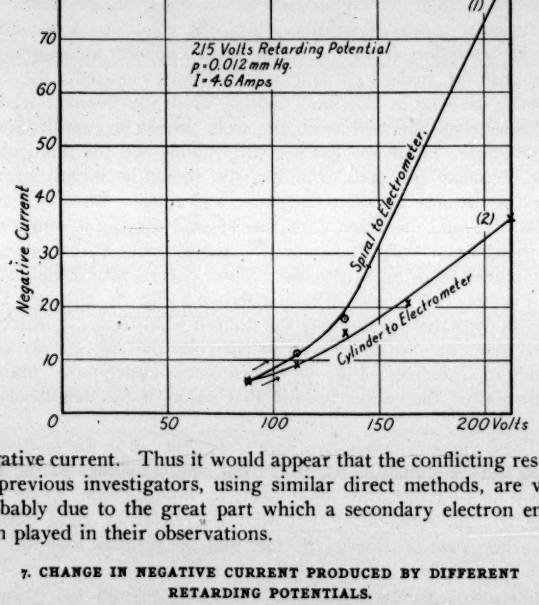
With this arrangement the predominant effects of an electron emission from the cylinder walls, spiral, and gauze, under bombardment, were clearly brought out in current-potential curves. The experimental conditions and arrangements were essentially the same as in those under classification (1), except that now current-potential curves were obtained when first the spiral and then the cylinder were employed as the collecting electrode. In this manner it was possible to show the effects of a secondary electron emission from the metal parts exposed to positive-ion bombardment, under experimental conditions essentially the same as those existing in Pawlow's work. With the *strong* retarding field, electrons liberated from the walls would be rapidly drawn to the gauze. With the gas pressure maintained for this experiment the mean free path of an electron should be slightly greater than the distance between the gauze and spiral. Many of these electrons would, however, penetrate beyond the spiral, and ionize gas molecules. For this reason this arrangement affords a sensitive indication of what occurs. Many curves were obtained in this manner, only one of which is shown (Fig. 7), although they were all consistent in showing the desired separation. For accelerating potential differences up to 85 volts the two curves were found to coincide. Fig. 7 shows very clearly the marked separation of the curves beyond that value in the neighborhood of 130 volts.

These curves confirm two points brought out in the discussion of the curves shown in Fig. 6. First, the proximity of the two curves up to about 130 volts seems to indicate that up to that value of the accelerating potential the electrons came mostly from the gauze $G'$, due to the fact that the positive ions did not reach the cylinder walls or spiral with sufficient energy to produce a noticeable secondary emission. Second, beyond 130 volts it would appear that electrons began to come from the walls of the platinum cylinder and spiral, as indicated by the marked separation of the curves, the current from the cylinder to the spiral being greater than that from the spiral to the cylinder. If the

negative current was due to ionization of the gas by the positive ions and not to secondary electrons, then the divergence of these two curves would be difficult to explain.

This experiment, though it does not entirely disprove the existence of a very small ionization effect by positive-ion impact, definitely indicates that a secondary electron emission from the walls is a primary factor, if not the entire source, of the observed

FIG. 7.




negative current. Thus it would appear that the conflicting results of previous investigators, using similar direct methods, are very probably due to the great part which a secondary electron emission played in their observations.

### 7. CHANGE IN NEGATIVE CURRENT PRODUCED BY DIFFERENT RETARDING POTENTIALS.

This investigation was a repetition of certain experiments carried out by Horton and Davies.[8] By varying the retarding field strength the distance into the ionization chamber which the positive ions travelled was varied. By measuring the increase in

the current to the collecting electrode for a given increase in the accelerating potential, in each case with different values of the retarding field, it was possible to provide a test for ionization by positive-ion impact, if such occurred to a measurable degree under the conditions of the experiment. Practically the same experimental results were obtained as those contained in the published article [8] of Horton and Davies and so are not shown here. Inasmuch as the increase in the measured current was *smaller* for the *smaller* value of the retarding *P.D.* in any two instances, when it should have been greater had the positive ions ionized the gas by collisions, it seems very clear that for the values of accelerating potential differences used that the positive ions do not ionize the gas to any measurable extent, at the gas pressures at which the experiment was performed 0.012 and 0.008 mm. Hg. The experiment does, however, definitely indicate that the predominant factor in the observed negative current is a secondary electron emission from the walls. If ionization of the gas by positive-ion impact existed, it must have been completely masked by the effects of this δ-ray phenomenon.

From the foregoing results it seems only logical, therefore, to conclude that resonance radiation likewise did not exist to any observable degree, since the two effects are so closely akin. Though repeated observations were made in a dark room, no radiation coming from the space between the disc *D* and the cylinder *C* could be seen.

## CONCLUSIONS.

The experimental results which have been described and discussed in this paper afford direct evidence:

(1) That the observed negative current in these experiments was due primarily to a secondary electron emission from the walls of the ionization chamber.

(2) That ionization of the gas by positive-ion impact did not exist to any measurable extent with gas pressures as high as 0.012 mm.

(3) That the secondary electron emission was produced by the impact of the positive ions with the walls of the ionization chamber.

(4) That it is possible that at relatively high pressures (above 0.012 mm.) the effects due to a gaseous ionization by positive-ion

impact might become an important factor relative to the effect of the δ-ray emission from the metal surfaces which existed in these experiments.

The conclusions drawn from these investigations contradict the interpretation given to Pawlow's work,[3] but confirm certain experimental results obtained by Horton and Davies.[8]

The spectroscopic and visual evidence of low "radiating potentials" contained in the work of Dempster[4] and Tate[7] certainly give very positive indications in favor of low "ionizing potentials" for positive ions. The fact that the known systems of uncharged atoms have normal energy levels lying between 4 and 25 volts, and that nearly all excited states differ from the ionized state by less than 6 volts[10] would certainly lead us to believe and expect that if a positive ion accelerated by a field produced by 5 volts could excite radiation by colliding with a hydrogen atom, then it could also produce ionization with a small amount of additional energy.

We are therefore led to the conclusion that ionization by positive-ion impact undoubtedly exists at potentials well within the range covered in these experiments, but that positive ions are such poor ionizers that direct effects produced by ionization of the gas at the lower pressures (0.012 mm.) are completely masked by secondary phenomena. The reason for this seems to be that the positive ions have a much greater efficiency in removing electrons from the metal walls (due probably to lower ionization potentials and the much greater number of atoms available) than from their relatively few collisions with gas molecules at lower pressures. This would seem to account for the conflicting results of existing evidence relating to ionization by positive-ion impact. It would likewise seem as though ionization potential measurements for positive ions in gases would have to be abandoned for measurements made at low gas pressures. At higher pressures, where the positive ions make relatively many impacts with gas molecules before striking the collecting electrodes, the secondary effects from the metal surfaces might be subordinated. One of the difficulties, however, which confronts one at higher pressures is the apparent impossibility of knowing the energy communicated to the positive ions by the applied accelerating potential, for at these pressures the positive ions have received their energy over several free

paths and thus have varying amounts of energy. The difference between the electron ionization and that produced by positive ions seems to be due to the fact that electrons are relatively efficient ionizers and a few collisions with gas molecules is sufficient to give a predominant gaseous ionization effect relative to the secondary effects from the metal surfaces. It would seem, therefore, that the hope of obtaining critical ionization potentials for positive ions must lie with investigations made at higher gas pressures, similar to Townsend's experiments on ionization of gases by electrons, and the author hopes to continue this work along the line indicated.

In conclusion the writer desires to express his thanks to Prof. L. B. Loeb, under whose direction the problem was undertaken. He also wishes to express his appreciation to Profs. E. P. Lewis and F. S. Brackett for their kind advice and suggestions made during the course of this work.

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DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA,
August 30, 1925.

**New Researches on the Magnetization of Ferromagnetic Substances by Rotation and the Nature of the Elementary Magnet.** S. J. BARNETT and L. J. H. BARNETT. (*Proc. Am. Acad. Arts and Sci.*, **60**, No. 2.)—Experiments conducted in 1914 by S. J. Barnett showed that "the rotation of iron, cobalt or nickel about a fixed axis in a magnetically neutral region at an angular velocity $N$ revolutions per second magnetizes the substance as it would be magnetized at rest by the application of an axial magnetic field with intensity $H_r = \lambda N$." The idea underlying this investigation came to him in 1909. Years later he found that John Perry in his "Spinning Tops" had recorded a failure to detect any magnetization of an iron rod produced by rotating it. The value of $\lambda$, the intensity of the field due to one revolution per second, was found to be $-3.6 \times 10^{-7}$ gauss. There are theoretical reasons for expecting a result about twice as great as this. Barnett later, using cold-rolled steel, nickel and cobalt, obtained somewhat greater values. Einstein and Haas in 1915 tried the converse experiment and made rods of magnetic materials rotate by applying a magnetic field parallel to the axis. From their observations they deduced a value of $\lambda$ about twice as large as Barnett's. Because of these differences in result it became desirable to repeat the work bringing to bear the experience gained in previous manipulation as well as useful criticisms that had been contributed.

Most of the new experiments were conducted in a non-magnetic laboratory at some distance from the main building of the Department of Terrestrial Magnetism of the Carnegie Institution in Washington. Great care was exercised in avoiding the presence of iron in the apparatus used. For instance, a magnetic separator was applied to the sand destined for a pier. Owing to the magnetic fields set up by electric railways the interval from 2:30 to 4:30 A.M. was deemed safest for the experiments. During the progress of the investigation there was a car-line put into operation throughout the two hours designated, but the Capital Traction Company substituted omnibuses in order to do away with the magnetic disturbance produced at a distance of five-eighths mile from the line. The effects of eddy currents and of the air-currents due to rotation were studied and eliminated. Indeed the list of errors sought and removed from influence upon the results is rather formidable. The metallic rods were rotated by an alternating current motor making about 30 r.p.s. Gear ratios from 2:7 to 2:1 were used.

Two kinds of steel, permalloy, Heusler's alloy, Preuss's alloy, cobalt and Armco iron were rotated. In all cases magnetic fields due to rotation were observed and measured. Moreover the value of the coefficient $\lambda$ was always close to its value found in the earlier experiments, and varied only a little from substance to substance. The weighted mean for gear ratio 2:1 is $3.78 \times 10^{-7}$, and for the ratio 1:1 it is $3.80 \times 10^{-7}$. Now that the coefficient is known to so high a degree of accuracy, it remains to develop a theory that agrees with the experimental results. G. F. S.

# THE SPARK BETWEEN CARBON RODS IMPREGNATED WITH A MIXTURE OF OXIDES OF MOLYBDENUM, TITANIUM AND VANADIUM AS THE SOURCE OF A CLOSELY SPACED LINE SPECTRUM IN THE VISIBLE REGION.*

BY

MARION EPPLEY, Ph.D.

Member of the Institute.

A SPECTRUM, made up of closely spaced lines extending over the entire visible region, frequently would be of use. The arc-spectrum of iron meets the above requirements when direct current of five amperes " or less " at one hundred and ten volts to two hundred and fifty volts is available.[1] Tube-spectra are conveniently produced, but in general have their lines too widely separated unless a limited region is considered.

A source giving a closely spaced line spectrum between λ6678 and λ3990 is the spark between carbon electrodes coated with a fused mixture of the oxides of vanadium, titanium and molybdenum. The lines, with but two exceptions (Mo 5896.12 and 5888.52) are of very nearly equal intensity. Thus it is not necessary to greatly over-expose strong lines in order to insure the appearance upon the plate of weak lines, the absence of the images of which would cause objectionable gaps. For the above reason, a narrow slit (about 0.03 mm.) and fairly long exposures (twenty-six minutes) produce excellent spectrograms. There is practically no continuous spectrum as in the case of the arc-spectrum of molybdenum.

In practice, the end of a graphite rod of suitable diameter (6 mm.) is heated to redness in the Bunsen flame and at once dipped into a dry powder of the following proportions by weight:

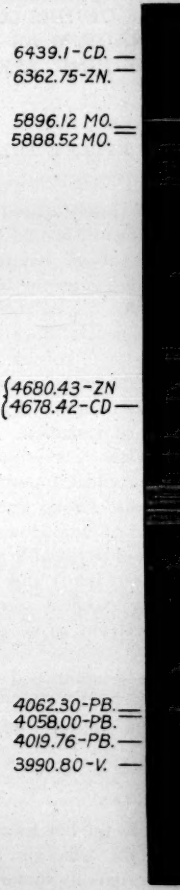
| | |
|---|---|
| Vanadic acid ($V_2O_5$) | 8 parts |
| Molybdic acid ($MoO_3$) | 5 parts |
| Anhydrous titanium oxide ($TiO_2$) | 2 parts |

A coating of powder adheres to the hot zone. The rod is heated again in the flame to fuse the adhering powder, which then impregnates the rod as well as coats its surface. These operations

* Communicated by the Author.

[1] MEGGERS, KIESS, and BURNS, Sci. Papers, Bur. Stand., 478, 264 (1924).

FIG. 1.


6439.1-CD.
6362.75-ZN.
5896.12 MO.
5888.52 MO.
4680.43-ZN
4678.42-CD
4062.30-PB.
4058.00-PB.
4019.76-PB.
3990.80-V.

are repeated until a black, heavy crust (with a rough irregular surface) encases the rod for at least a centimetre from its end. Two such rods serve as electrodes. They may be cut to a wedge before coating, with advantage to the steadiness of the spark, which, by this well-known device, can be made to confine its shifts to a back and forth travel along a line in the plane in which lie both the slit and the optical axis of the collimator.

The above treatment produces an electrode that will last for a sparking of thirty minutes or longer, under ordinary conditions.

The spectrogram herewith was taken with a Hilger constant-deviation spectrograph upon a 3¼-inch by 4¼-inch Wratten and Wainwright panchromatic plate. The slit-opening and time of exposure were 0.03 millimetre and twenty-six minutes, respectively. The spark was generated by current from a transformer rated at fifteen thousand volts, operated from the one-hundred-and-ten-volt, sixty-cycle service line. The current through the primary was four amperes. A condenser was in parallel with the spark-gap, and a coil having an inductance sufficient to eliminate "air lines" in series with it.[2] The spark-gap was about one centimetre in width. Light from the full length of the spark was focussed upon the slit by means of a sphero-cylindrical lens. This plate is characteristic.

To identify the lines of this spectrum it is convenient to photograph upon it the spark-spectrum of an alloy of the following composition by weight:

| | |
|---|---|
| Cadmium | 35 parts |
| Zinc | 35 parts |
| Lead | 73 parts |
| Tin | 30 parts |

This combination has the advantage over that of Hartley[3] that the cadmium line λ6439.1 and the zinc line λ6362.75, the cadmium line λ4680.43 and the zinc line λ4768.42, and the two lead lines λ4062.30 and λ4058.00, are so placed as to make their identification an easy matter. It has the further advantage that its principal lines photograph with approximately the same intensity. The lines are also satisfactorily situated for the application of Hartmann's Formula.[4]

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[4] HARTMANN, *Astrophys. Jour.*, **8**, 218 (1898).

**Atomic Theory and Mechanics.** N. BOHR. (*Nature*, Dec. 5, 1925.)—This paper serves to make clear the immense difference between the atom of the time of Maxwell and the atom of to-day, with its quantum theory and correspondence principle. The nucleus of the atom with its electrons held in leash seemed complicated enough, yet, because it resembled a miniature solar system, it presented itself under a somewhat familiar aspect just because of its similarity to that system whose laws have been so completely worked out on the basis of classical mechanics. We are warned in this paper that too much must not be expected from the analogy to the solar system. The atom must possess a stability that does not exist in the solar system. Besides this a planet has a possibility of continuously varied motion that an atom must be without, if it is to explain the sharply defined properties of the element to which it belongs.

The application of the quantum theory to physical phenomena leads to results subversive of some of our cherished conceptions. "One is faced not with a modification of the mechanical and electrodynamical theories describable in terms of the usual physical concepts, but with an essential failure of the pictures in space and time on which the description of natural phenomena has hitherto been based." It is in such a manner that Heisenberg has formulated the problem of the quantum theory. "In contrast to ordinary mechanics, the new quantum mechanics does not deal with a space-time description of the motion of atomic particles. It operates with manifolds of quantities. . . . These quantities satisfy certain relations which take the place of the mechanical equations of motion and the quantization rules."

Another sacrifice demanded by quantum mechanics is the abandonment of mechanical models so dear to the heart of the Anglo-Saxon physicist, of which Sir Oliver Lodge made such extensive and happy use in his "Modern Views of Electricity" a generation ago. In the new formulations required by the quantum theory the results derived from higher algebra find application. Thus the proofs of certain theorems are founded on the theory of matrices developed by Cayley and Hermite. "It is to be hoped that a new era of mutual stimulation of mechanics and mathematics has commenced. To the physicist it will at first seem deplorable that in atomic problems we have apparently met with such a limitation to our usual means of visualization. This regret will, however, have to give way to thankfulness that mathematics, in this field, too, presents us with the tools to prepare the way for further progress."

This paper was delivered at the Sixth Scandinavian Mathematical Congress in Copenhagen last August. G. F. S.

# THE APPLICATIONS AND MECHANICAL CALCULATION OF CORRELATION COEFFICIENTS.*

BY

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STATISTICS is the application of mathematics to the social sciences. It is the method for quantifying complex social phenomena, and attempting to reduce their relationships to mathematical formulæ which will permit us to predict and control the phenomena. Perhaps the most general problem in science is the search for relationship between phenomena. We never know the intrinsic nature of a thing but only progressively define it as we know more and more of its relationships to other things. To learn these relations in physics or chemistry, we can experimentally vary the conditions one at a time and observe the resulting co-variation of whatever phenomena we are studying. But we cannot experiment as easily in social, economic, educational and many psychological and biological investigations. If we wish to experiment upon the effect of fertilizer on crop yield, we cannot keep the rainfall conditions constant as yet. We are forced to observe a large number of instances of varying fertilization and resultant bushels per acre and then select for study only those instances in which the rainfall has been equal. (I will speak of another method of accomplishing this control through selection by means of partial correlation later.) If in addition there are many factors to be controlled, such as chemical constituents of the soil, amount of cultivation, quality and spacing of seeds, they may require still further selection. It can readily be seen that one must have a very large number of observations in order to have an adequate sample after several successive selections.

When we have controlled as many of the experimental factors as possible by selection, we can proceed to explore for relationships by means of correlation. The correlation coefficient tells us to what extent two variable phenomena or characteristics are related. It is the measure of the tendency to co-vary or the tendency of

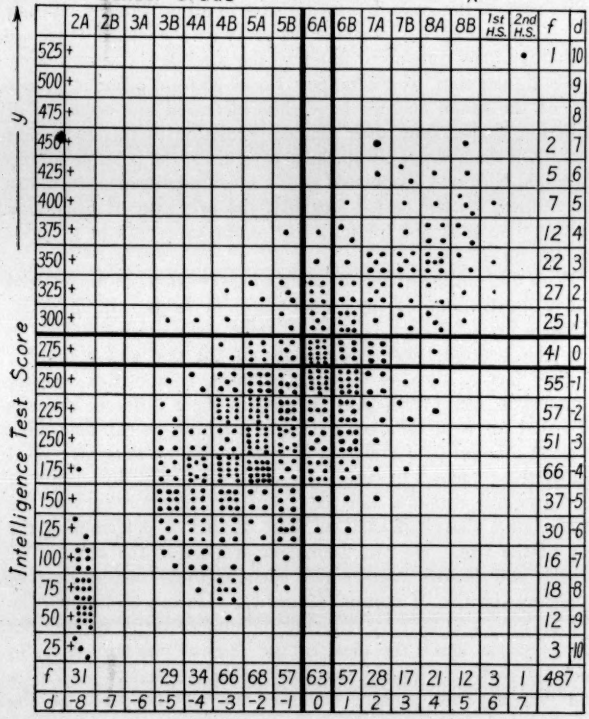
* Presented at a meeting held Thursday, January 14, 1926.

two functions to be associated somehow. Since in complex phenomena clean-cut co-variation is never found, we can only determine the amount of the *tendency* of two things to co-vary or to be associated with each other in some way. There are many ways of looking at the correlation coefficient. In addition to being an index of co-variation or correlation, it can, under some special conditions, be regarded as the percentage of common elements or common causes in the two phenomena studied. The meaning of the correlation coefficient can perhaps be most conveniently illustrated by a scatter diagram of the observations, such as in Fig. 1. Here the horizontal axis represents the different degrees of the $x$-variable, which is the grade to which children have attained in school. The $y$-variable along the vertical axis represents the intelligence test scores of those children. If there is high correlation the scatter of points will tend to cluster along a straight diagonal line. That means that for every unit of increase in grade attainment there will be proportional increase in intelligence test score. If there is low correlation, or if there are many other factors besides intelligence determining school attainment, then the observed points in the scatter diagram will be found in a rough circle covering all four quadrants. This means that any intelligence score would be observed associated with any grade position and that there is therefore no observable association. This is zero correlation while the grouping along the diagonal line represents perfect correlation of unity. Intermediate degrees of positive correlation are expressed by decimal coefficients between 0 and 1.00. The correlation coefficient of Fig. 1 is .76.

We can go further than merely correlate or test for the presence of relationship. We can use correlation for prediction. This prediction is subject to limits of error or may be expressed in terms of increasing probability which are proportional to the size of the correlation coefficient. Thus, given the intelligence test score of a child, for example the value in the middle row, 275+, we can predict his most probable school grade, 6A, as being the mean of the grades in that row. This predicted value is stated as that mean, 6A, plus or minus its probable error (one full grade) which is a measure of the dispersion of the observations about their average. More precisely the probable error is that amount which includes half the cases or that value within which the probabilities are 50–50 that a given case will fall. It may read-

ily be seen that as the correlation increases the observed points will constrict more narrowly towards the diagonal line of relationship, and the scatter of cases on either side of their mean will shrivel

FIG. 1.




$r = .76 \quad \sigma_x = 3.07 \quad \sigma_y = 8.78 \quad N = 487$

Correlation scattergram.

up towards the centre. This means that the probable error of the predicted value will become smaller or that the prediction increases in precision and certainty. We can express this effi-

ciency of prediction as a percentage and call it $E$. It will vary from zero efficiency with zero correlation or prediction based on pure chance to 100 per cent. efficiency of prediction with correlation of unity. The formula for $E$ is $E = 1 - \sqrt{1 - r^2}$. $E$ is the percentage reduction in the total range of possible occurrence. It is that part of the scale in which a case in all probability will not fall. Thus in Fig. 1, if we take the array of $Y$ marked 250±, we see that the cases only occur in ten of the possible sixteen columns. This is 63 per cent. of the range. Cases will not occur in 37 per cent. of the range and we have thus increased our accuracy of prediction 37 per cent. over chance prediction in this particular array. On the average of all the arrays, then, the possible grades that might be found, associated with a given intelligence score, has been reduced 35 per cent. Actually, the precision of prediction is better than that, for the majority of the cases will be grouped near the mean.

With this outline of the meaning of correlation, let me proceed to give illustrations of its use in different fields. In industry, suppose a manufacturer of some product, such as tires, wishes to know the relation between longevity of the tire and a number of other factors such as weight, thickness, composition, quality of materials, etc. With tires varying in these different respects and tested for wear on a road friction machine, he can determine the exact amount of correlation or dependence of longevity upon each of these factors in turn. He can even assign by means of the regression equation derived from the intercorrelations the exact relative shares of each of these factors in determining the wear of the tire. He can thereupon proportion the amount of research and factory costs which each of these factors deserve to produce the tire of optimal longevity. He can strengthen the weak features and save by reducing the unnecessarily strong ones until he might reach the ideal of the famous one-hoss shay, in which no part was weaker than any other, so that it lived to a good old age and finally collapsed in all its parts at the same moment.

In insurance, all the different indices of health, such as blood-pressure, previous sicknesses, chemical tests, age, occupation, etc., may be correlated against length of life. From this calculation we may afterwards predict within known limits of error the most probable length of a man's life as far as these health indices

represent factors which determine the length of life. There are probably a number of gentlemen here this evening, from whose fields I am drawing illustrations, who could tell us much more precisely of the use of correlation coefficients in their problems. I hope that I shall not misrepresent them and that they will supplement these suggestive illustrations later.

An example might be drawn from the field of politics which has as yet been only very slightly quantified. Suppose some large civic and research foundation wished to determine precisely the factors determining the election of mayors, in the interests of improving municipal administration. From some large group of towns in a given region, data on the mayors elected and candidates defeated over a period of years might be collected, including such items as age, length of training in public life, number of times previously appearing on ballots, education, race, and religion, campaign budget, and indications of strength of the party organization, such as frequency of meetings between elections, number and value of "plums" distributed by the party coming into power, etc. Through multiple correlation, which is the correlation between one variable and a group of several others, we can determine the influence of the combination of all these factors upon election to the mayoralty. We may write the regression equation assigning the shares to each of these influences and determine the share of the unknown or as yet unmeasured residual influences. With this equation a civic organization might pick its most able potential candidates and decide amongst them by fitting his specifications into the equation and determining each candidate's probability of election.

An illustration from financial realms might be taken from the stock market. We wish to predict the course of a given stock or group of stocks. We may collect data or indices of their strength. We can, by a rather laborious multiple correlation technique, predict the most probable course of a given set of stocks. The limitations to this are that the available data represent only a small part of the influences at work in determining prices, and that the statistical procedure is complex and laborious. It may, however, be worked very successfully by competent people in the stock market, when proper allowances have been made for improbability, large enough number of cases, long enough periods of time, and temporary and unusual disturbances such as the failure

of the French debt negotiations, unexpected change in the rediscount rate, and other less obvious influences which do not appear in the regression equation.

From all of these illustrations, one should not get the impression that we can predict with too great precision. Correlation simply enables us to determine the amount of relationships present in our data. The fundamental and far more difficult problem is to get good data. To get good data means to measure the subtle and intangible causes which determine (and so have high relationship to) the phenomena whose behavior we wish to predict and control.

In biological research we may correlate the relative influence of heredity and environment in producing the final integrated organism. We may control heredity by parthenogenetic multiplication of a single ovum and then deliberately vary the environmental conditions of temperature, humidity, nutrition, stimulation, grafting or extirpation, and correlate on large numbers of such organisms the resulting conditions with the environmental variations. Conversely, we may keep constant environmental conditions and vary the heredity by taking different ova from different parents. We may even make a slight first approximation towards this sort of experiment in the education of human beings. For example, in a project we were executing for the National Research Council, it was desired to get intelligence tests which would measure predominately those factors making for achievement in school, which were hereditary or due to native ability. All the orphanages in the eastern United States were canvassed to find the one in which experimental conditions of common environment from as early childhood as possible could be secured. Then with environmental differences partially controlled in this way, we sought to predict achievement in school and felt that those tests which would predict that achievement were measuring differential native ability factors, at least a little more purely than where environmental training was completely uncontrolled.

In research in higher education it has been found that college admission examinations, based on preparatory school work for men admitted, have an efficiency of prediction of their attainments in college courses of about 12 per cent. (when $r = .45$). Intelligence tests have about an equal efficiency. The school records of the men have a slightly higher efficiency. But each of these

three indices measures some factors not sampled by the others. Consequently, we find that when they pool their prediction by means of multiple correlation, we increase that efficiency of prediction from 12 per cent. up to 29 per cent. ($r = .70$). In the same way in industry, if a good criterion of success on a job can be had, a diversity of measures correlating with it can be found with sufficient research. The prediction by the employment department of an applicant's future success can be progressively raised in precision.

These efficiencies may seem ridiculously low compared with that possible in the physical sciences. It must be remembered, however, that predictions we have been making in the past on such things and considered good by sheer opinion and subjective observation were even lower. It emphasizes the fact that in social phenomena there are still a vast number of unmeasured influences at work which await further research.

Correlational techniques are all of very recent development, principally in the last fifteen years, and have already diversified until their name is legion. There is rectilinear and various types of curvilinear correlation. There are many approximative as well as very exact formulæ. There are graphical and algebraic, tabular and mechanical methods of solving the formulæ in considerable number. There are further complications of correlation, such as multiple and partial correlation.

There are a great number of conditions or qualifications which must be observed in their use and in their interpretation. The popular fallacy that " anything may be proved by statistics " arises from not observing these limiting conditions. I might mention two of these limitations. One is the question of adequacy of sampling. One test for that is known as some variety of reliability correlation. Thus we may have taken observations on some group and we need to compare the results with an equal number of observations on another similar group. A difference in averages of the two samples, if large enough to be significant, indicates a constant difference of some sort. A low correlation coefficient between the observations in the two samples indicates all sorts of variable influences which are not co-varying or similar in the two samples. Consequently it is always desirable to know the reliability correlation coefficient or the correlation

between two samples of each of the phenomena correlated before we base other calculations upon it.

Another precaution is to know the range or variability of the distribution of the two things correlated. The correlation between ability and achievement of all grade school children will be very much higher because their range is longer than a similar correlation on a fifth grade group where the range both of achievement and ability is smaller. Again, in Fig. 1, the cases in any one array are less widely scattered than in the sum of all the arrays. It is similar to reducing the labor costs of a large and small firm to percentages of total cost before they can be compared. In the same way we need to transmute by appropriate formulæ, correlation coefficients to coefficients based upon the same or standard ranges in order to compare amounts of relationship.

So far I have spoken principally of simple correlation between variables two at a time. The relationships amongst a large number of variables may be analyzed by partial correlation. A partial correlation coefficient indicates that *part* of the correlation between two variables which is independent of the simultaneously varying influence of one or more other variables. These others are then said to be controlled or partialled out.

In the former agricultural illustration we wish to determine the direct dependence of crop on fertilizer when rainfall, which inevitably varies at some time, is controlled or partialled out. We might correlate crop and fertilizer on only those instances where the rainfall was ten inches, then again where it was twelve inches, and again for fourteen inches, and so on. We might then average these coefficients, each one of which is obtained for constant rainfall. But we can do this more conveniently by partial correlation. By a simple formula involving the observed or zero order correlation coefficients, we may build up successive orders of partial correlation controlling or partialling out as many extraneous variables as we may have measured. (This requires many cases as the probable error increases with each order!) Thus we may learn the relation between fertilizer and crop, independent of rainfall, soil, chemistry, and other factors.

From these illustrations of the applications of correlations, let us turn to their mechanical calculation.

Before describing the machine which is illustrated in Fig. 3, let us review the arithmetic involved, so that you may see the

purpose of all the wheels later on. Fig. 2 is a sample correlation calculation. We start with two series of numbers or observations—an $X$ series and a $Y$ series. The problem is to determine the amount of correlation between them, or how much they tend to co-vary. We first get the mean of each series by listing on an adding machine or otherwise. Next, in the small $x$ column we enter the deviations of each raw score from the mean of the $X$

FIG. 2.

*Arithmetic of Correlation.*

(Rectilinear; Product Moment Method.)

| Variable $X$ | $*x$ | $x^2$ | Variable $Y$ | $*y$ | $y^2$ | $xy$ |
|---|---|---|---|---|---|---|
| 2 | −5 | 25 | 8 | 0 | 0 | 0 |
| 4 | −3 | 9 | 5 | −3 | 9 | +9 |
| 6 | −1 | 1 | 7 | −1 | 1 | +1 |
| 13 | +6 | 36 | 9 | +1 | 1 | +6 |
| 10 | +3 | 9 | 11 | +3 | 9 | +9 |
| | 0 | 80 | | 0 | 20 | 25 |
| | $\Sigma x$ | $\Sigma x^2$ | | $\Sigma y$ | $\Sigma y^2$ | $\Sigma xy$ |

$\text{Mean}_x = \frac{\Sigma_x}{N} = 7$ $\qquad M_y = 8$

$S.\,D_x = \sqrt{\frac{\Sigma x^2}{N}} = 4$ $\qquad S.\,D_y = 2$

$r_{xy} = \frac{\Sigma xy}{\sqrt{\Sigma x^2 . \Sigma y^2}} = .625$ or $\frac{N\Sigma xy - \Sigma x \cdot \Sigma y}{\sqrt{N\Sigma x^2 - (\Sigma x)^2}\ \sqrt{N\Sigma y^2 - (\Sigma y)^2}}$

For true mean as above For arbitrary origin

$$E = 1 - \sqrt{1 - r^2} = 22 \text{ per cent.}$$

series. In the next column we enter the squares of these deviations. Similarly we get the algebraic deviations and their squares for the $Y$ series. In the last column we get the cross-products of each $x$ deviation times its paired $y$ deviation. Then we must get the sums of these columns. These six sums—$\Sigma x$, $\Sigma x^2$, $\Sigma y$, $\Sigma y^2$, $\Sigma xy$, $N$—are the ingredients which are combined in the formula for $r$, the correlation coefficient given below. In case we know the true mean, the formula is simple. In case we do not know the true mean, or if it is a decimal value, we use an arbitrary origin and apply a precise correction factor later on. The formula involving the arbitrary origin is the second more complicated one.

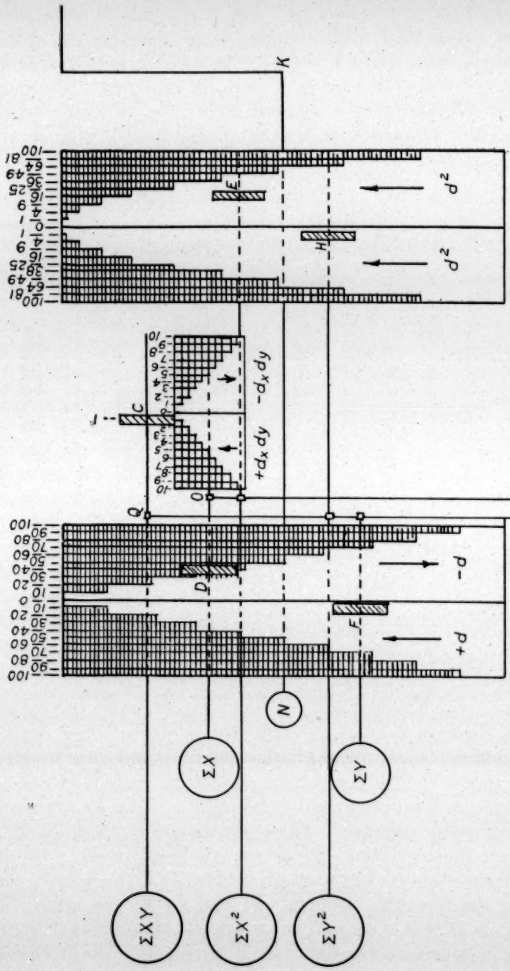
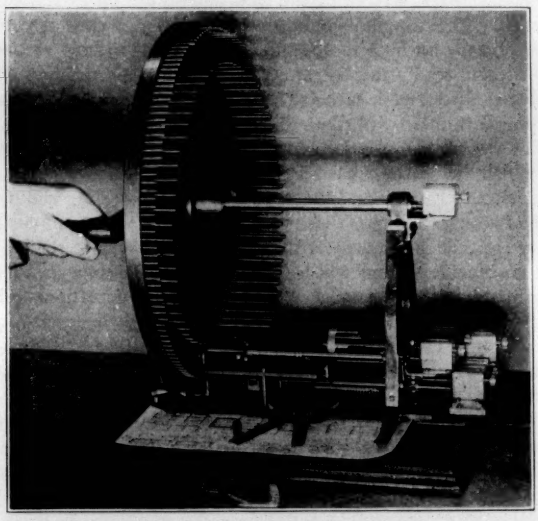



FIG. 3.

Correlation machine diagram.

The labor involved in getting these six sums is very great and there are numerous tables, graphs and other short-cut devices that have been put out in the last few years. There are two machines for this purpose with which I am acquainted. One is a correlation and forecasting machine developed by Professor Hull, at Wisconsin, and the other one is this machine which I have

FIG. 4.



Preliminary model A of the correlation machine.

developed at the Princeton Laboratory. They are mutually supplementary, designed for different classes of problems. His is for the Pierce-Arrow trade—this one for the Ford.

This model (Fig. 4) is a preliminary one with many inadequacies which we hope to eliminate in the model we are now constructing. This later model is diagrammed in Fig. 3. To begin a calculation, we group the variables into class intervals, and enter these on the slip of paper under the setter arms. The operator then sets the $X$ arm and the $Y$ arm at the appropriate class intervals and turns the crank. This enters the six sums in

the six counters at the right. The $X$ control arm through a gear and rack moves the $X$ pinion to any one of twenty-one banks of teeth. In each of $d^2$ drums there are ten banks of teeth, each containing as many teeth as there are units in the successive squares of the numbers from 1 to 10. There is one of the widest tooth across the whole face of the drum, four (including the first) of the next width, nine (including the previous four) of the next shorter, sixteen of the next and so on, up to 100 of the shortest. The $X$ square counter registers one for each arm of its pinion that is hit by a tooth, and therefore records the square of the $X$ value set by the operator. The $+d$ and $-d$ drums contain ten banks of ten teeth each. The $X$ counter, which is actuated by the pinion in mesh with these drums, counts one for each revolution or for every ten teeth. Thus it is counting the number of units for which the operator has set the $X$ control. Simultaneously and similarly the $Y$ units and the $Y$-square units are being cumulated in the two $Y$ counters. This model will enable the use of the true mean (if that is known) with positive and negative deviations. The positive deviations will be turned into the counter in a clockwise manner from drum $+d$, while the negative deviations will be turned out of the counter through counter-clockwise rotation of the pinion. This reversal of the rotation will be accomplished through having the two duplicate right- and left-hand drums, $+d$ and $-d$, geared to go in opposite directions. From either one of them the pinion may take rotation, according as the setter arm is set above or below the midpoint of its scale.

The $xy$ products are accumulated through the $+d_x d_y$, $-d_x d_y$ mechanism. The $+d_x d_y$ drum is mounted rigidly with the $x$ pinion, $D$, and is therefore making as many rotations as there are units of deviation in the $X$ score being entered. It is also going in the clockwise or counter-clockwise direction according to the sign of the $x$ deviation. The duplicate $-d_x d_y$ drum, through an intermediate gear, is always going in an opposite direction to the $+d_x d_y$ drum. The $xy$ pinion, $C$, can take rotation from either drum according to the sign of $y$ and will take rotation from that bank of teeth which corresponds in number to the units of deviation in the $Y$ score. Thus at each rotation of the crank shaft the $+d_x d_y$ drum will revolve $x$ times and on each revolution will drive the $C$ pinion $y$ teeth, thus achieving the rotation of $x$ times $y$ teeth of the $C$ pinion and the entry of $xy$ units in its counter.

The $xy$ counter then accumulates the values algebraically. Whether the $x$ deviation is plus or minus or the $y$ is plus or minus, all the four possible combinations of signs are allowed for and properly entered in the $xy$ counter. A little counter on the drive shaft cumulates $N$ or the number of cases entered.

The model in Fig. 3 instead of having the $X$ and $Y$ values entered in by radial setter arms will have a scatter diagram plotting device. This consists of two arms at right angles, one with the $X$ scale written along its edge and the other with the $Y$ scale along its edge, and with a writing point at their junction. With coördinate paper underneath, the operator slides the writing point to the intersection of the pair of $X$ and $Y$ values, as if he were plotting the points in Fig. 1, and turns the crank. *This yields both the geometric plot with all the information of individual variations afforded by it and the algebraic coefficient summarizing the amount of relationship in a single number.*

As by-products, the means and standard deviations of both series are secured. The curvilinear correlation ratio, eta, may be calculated as also bi-serial correlation. A further feature is the possibility of taking trial runs, that is, by adding or subtracting cases to find all the above coefficients for differing population samples and so testing for adequacy of sampling. For if the coefficients do not vary as more cases are entered in, it is an indication that a representative sample has been secured.

With a Monroe calculator the formula in the case of the arbitrary origin may be solved in about forty-five seconds from the readings on the dial faces. With the simpler formula when using the true mean, it may be solved in fifteen seconds or the operator may solve it roughly mentally and so be able to watch the stability of the coefficient as he enters more cases.

As the appreciation of the usefulness of properly controlled statistical work in social and biometric fields grows, the amount of such calculation is already increasing in geometric ratio. It is hoped that a mechanical correlation device such as this will greatly reduce the laboriousness of such calculations and also enable much more research in the statistical sciences.

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**Atoms and X-rays.** F. W. ASTON. (*Nature*, Dec. 19, 1924.)—Prout held that the atoms of all elements were built up of atoms of hydrogen. Dalton maintained that all atoms of the same element had the same weight. "If both these theories were right, the atomic

weights of all elements would be comparable with each other as whole numbers. This the chemist soon found was incompatible with experimental evidence. They had to choose between the two theories and choose the one that was untrue. In this they were perfectly right, for it is more important that a scientific theory should be simple than that it should be true."

The truth of Dalton's postulate cannot be tested by chemical means directly, since the chemist deals with immense numbers of atoms. He cannot sort out his atoms to see whether all possess the same atomic weight. Just this distinction can, however, be made by the use of positive rays, which consist of positively charged atoms moving with high speed. A table is then given showing the results of positive-ray analysis for no less than fifty-six elements, that is, for those of atomic numbers 1 to 40, 47 to 60 and 80 to 83. As there are eighty non-radio-active elements, it is seen that the work of analysis is moving toward completion, though many difficult elements remain to be examined. Of the fifty-six elements tabulated, about twenty-six have been found to be simple; they are made up of atoms of one kind only. Among them are H, C, N, O, Al, Mn, Y, and Bi. All the rest of the elements investigated have atoms of two or more kinds. "Selenium, krypton, cadmium and mercury each have six, tin probably eight and xenon possibly nine isotopic constituents." Except in the case of hydrogen the weights of all atoms studied come out whole numbers to one part in a thousand. The greater atomic weight of hydrogen, 1.008, is due to the absence of close packing in the structure of the hydrogen atom. This atom consists of one proton in the nucleus and one electron circulating around the nucleus. A helium atom, on the other hand, has a nucleus composed of four protons and two electrons and has two electrons in orbits. Thus the helium atom has four times as many protons and four times as many electrons as the hydrogen atom. Yet its weight is not $4 \times 1.008$ but is exactly 4. It is to the manner in which the protons and electrons are arranged in the helium atom that the loss of mass is to be ascribed. If one gram of hydrogen could be converted into helium and the mass that disappears be changed into energy, it would amount to 200,000 kilowatt-hours.

The author examines the claims recently made for the transmutation of mercury into gold and rejects them on theoretical grounds.

An excellent idea of the dimensions of an atom comes from the following comparisons: "Were we to construct a scale model of the atom as big as the dome of St. Paul's, we should have some difficulty in seeing the electrons, which would be little larger than pinheads, while the protons in the nucleus would escape notice altogether as dust particles invisible to the naked eye. If we represent the nucleus of a helium atom as the size of a pea, its planetary electrons would be about a quarter of a mile away. An atom, even of so heavy an element as lead, is as empty as the solar system." G. F. S.

# A NOTE ON THE CATHODE-RAY OSCILLOGRAPH.*

BY

JÛICHI OBATA.

In the December issue of the Journal of The Franklin Institute Mr. F. Richard Terroux, of the McGill University, published a result of experiments, which shows that the use of a fluorescent screen deposited on a quartz window might greatly simplify the operation of the cathode-ray oscillograph and so extend its applications.

The present author, working some time with the Wood's type cathode-ray oscillograph with the object to apply it for the study of transient phenomena, has made some experiments to improve its ability, and should like hereby to make some further remarks on it.

One of the serious drawbacks of the cathode-ray oscillograph lies in the fact that it is a matter of considerable difficulty to obtain high photographic sensitivity, making it at the same time highly sensitive electrically.

Mr. Terroux devised a tube with a quartz window, so as to place the photographic plate outside the tube and to dispense with the labor of evacuating the tube constantly.

In his tube a *cold* aluminum cathode was, however, placed about 10 cm. apart from the anode and an induction coil was employed to operate the tube. The working potential in this case must have therefore exceeded several thousand volts or still more, making the photographic sensitivity of the beam so great as to give a fine impression on a dry plate placed outside the tube even with an exposure less than one-hundredth of a second.

Mr. Terroux describes nothing about the electrical sensitivity of his tube. Inasmuch as the velocity of the electron forming the cathode beam is proportional to the applied voltage, the electrical sensitivity of his tube may be estimated to be far inferior to those of the oscillographs devised by Johnson and Wood, so that its use should be limited to some kind of problems.

The present author, working with the Wood's type oscillograph, has experienced considerable difficulty in obtaining good

* Communicated by the Author.

records of transient phenomena, even when using the very expensive Schumann plates sensitized with calcium tungstate and supplied by Adam Hilger and Company, London.

In order to dispense with the Schumann plate a thin quartz plate, 3 × 5 cm. and 0.4 mm. thick, covered with a thin layer of calcium tungstate, was placed on the ordinary special rapid plate inside the camera of the oscillograph.

The results show that by this method the sensitivity for the cathode beam of the ordinary dry plate can be somewhat improved, but it is still inferior to the Schumann plate sensitized for the use of cathode-ray work.

It may therefore be thought that if a quartz window was used in a tube, which is made electrically high sensitive by the use of a heated cathode and by operating with low voltage, the intensity of the cathode beam after passing through the thick quartz window would not be sufficient for recording transient phenomena on a dry plate.

Thus, the difficulty of obtaining high electrical and photographic sensitivity at the same time still remains.

PHYSICS DIVISION,
AERONAUTICAL RESEARCH INSTITUTE,
TOKYO IMPERIAL UNIVERSITY.

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**The Transparency of Water to Ultra-violet Light as an Indication of Its Potability.** J. DUCLAUX and P. JEANTET. (*Comptes Rendus*, Nov. 3, 1925.)—Chemically pure water for lengths of 10 cm. is transparent to wave-lengths as small as 1900 Å., *i.e.*, well down in the ultra-violet. "It is remarkable that all the substances ordinarily found in what is called pure water, that is to say mineral salts, fail to diminish sensibly this transparency, provided that their concentration does not exceed that usually occurring in springs. On the other hand, substances under suspicion, that water may contain, render it opaque and in general the more so, the more serious or the more recent the contamination which they betray." Ammonia, proteins and albumin show their presence by increased absorption in the ultra-violet. Sewer water, stagnant water and water from house drainage, all show opacity, even after being filtered. Well water from different sources, though transparent and colorless, distinguishes itself from pure water by its absorption. Water from a stream that has passed through a small town is more opaque than a sample taken above the town. Strangely enough rain water is opaque in the extreme ultra-violet. The cause of this is not known.

G. F. S.

## NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

### RACK MARKS AND AIRBELL MARKINGS ON MOTION PICTURE FILM.[1]

By J. I. Crabtree and C. E. Ives.

UNLESS precautions are taken in the development of motion picture film by the rack and tank systems, more development takes place where the film passes over the slats at the top and bottom of the rack and bands of greater density known as rack marks are formed. These markings are caused by convection currents of exhausted developer and consequential retardation of development of the film along the sides of the rack. Rack marks may be prevented by: (1) Agitation of the developer; (2) agitation of the rack either by a re-immersion or a "square motion" method; (3) movement of the film along the rack during development by using rollers at the ends of the rack or progressing the film manually; (4) the use of broad end slats with curved surfaces; and (5) development to completion. Rack marks are also produced in a weakly acid fixing bath due to the continuation of development, while markings may be caused when toning film on a rack in a single solution toner.

Airbells which cling to the film as the rack is immersed in the developer cause white spots due to the local protection against development or fixation given by the bubbles. The shape and configuration of airbells is described and an illustrated classification of six types of markings is included. The factors affecting the formation of airbells are: (1) The manipulation of the rack; (2) the quantity of grease on the film; and (3) the condition of the developer. Airbells may be prevented by: (1) Soaking the film in water or a 2 per cent. sodium carbonate solution before development; (2) the avoidance of the use of old developer; (3) slow immersion of the rack; (4) allowing the film to remain under the surface of the developer after the first immersion for at

* Communicated by the Director.

[1] Communication No. 250 from the Research Laboratories of the Eastman Kodak Company and published in *B. J. Phot.*, **72**, 775, 1925.

least thirty seconds before lifting the rack out; and (5) mechanical removal of airbells.

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**Transmutation of Elements.** A. SMITS, University of Amsterdam. (*Nature*, Jan. 2, 1926.)—The greatest care was applied to free the apparatus from any suspicion of mercury. The vacuum desired was obtained by using a pump that employed no mercury. The quartz parts of the lamp were cleaned chemically, steamed and then heated to redness. The metallic parts underwent the same treatment. The lead betrayed no trace of mercury or thallium. All the materials gave no spectroscopic evidence of containing either of these two metals.

The electric current passed through a lamp in which lead kept molten replaced the mercury of the mercury-vapor arc lamp. When 40 amperes passed "the result was that, whilst initially the lead spectrum showed only very weakly the mercury line 2536 in the ultra-violet, after ten hours' burning the strongest mercury lines had appeared in the visible as well as in the ultra-violet part of the spectrum, and also the most characteristic thallium line, indicating a transmutation of lead into mercury and thallium." Later, for a continuous current was substituted a series of sparks of higher current strength, namely, 60 amperes. "After nine and one-quarter hours' sparking all mercury lines, even the very weak ones, were present." A series of reproductions of spectra is given, in each of which the spectrum of mercury is compared with the spectrum of the lead. In the first when the lead has not been subjected to the discharge no mercury lines appear in the lead spectrum, though the author says that in the negative there is a trace of the mercury line 2536, which was the first to put in an appearance in the experiments. Then as the discharge was sent through the lamp for longer and longer durations the mercury lines grow in prominence.

A second method confirmed the formation of mercury from lead. Between two electrodes of pure lead, mounted 4 mm. apart and separated by a liquid dielectric, sparks passed for twelve hours under a pressure of 100,000 volts. From the dispersed lead, mercury was driven off by heat and by iodine vapor was turned into red $HgI_2$. This reaction was distinctly obtained by using the dispersed lead but could not be gotten at all from the electrodes. The author is seeking to discover whether thallium also is formed by this second method. He announces his purpose of applying both of his methods to bismuth and thallium as well as to other metals. G. F. S.

## NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

### THE HYDROGEN ION IN BEET-SUGAR WORK.[1]

By R. T. Balch.

[ABSTRACT.]

THE methods and principles used in hydrogen-ion concentration measurement, with particular reference to control of beet-sugar manufacture, are briefly reviewed. Both electrometric and colorimetric methods are described. Of the former, the use of tungsten or similar electrodes in conjunction with a recording potentiometer appears to be most promising, as there is a possibility of establishing with such equipment an automatic control of carbonation processes. An attempt was also made to find suitable indicators that could be used in the various colorimetric methods for the pH range between 9.5 and 14.0. Only three dyes out of twenty-one tested might possibly have an application, namely, tropaeolin O (resorcin yellow), No. 143, pH range 11.1–12.4; thymolphthalein, pH range 9.3–10.6; alizarin yellow GG No. 48, pH range 10.0–11.6.

### DETERIORATION OF COMMERCIALLY PACKED CHLORINATED LIME.[2]

By C. C. McDonnell and Leslie Hart.

[ABSTRACT.]

IT HAS long been known that the strength of chlorinated lime decreases with age. Since its activity as a germicide depends upon its available chlorine content at the time of use, this deterioration is very important to consumers. The Bureau of Chemistry accordingly undertook an investigation to determine the loss of available chlorine in bleaching powder, when stored in containers of various types under different conditions of packing and temperature.

This investigation showed that in general the keeping qualities of the bleaching powder were not greatly affected by the type and

* Communicated by the Chief of the Bureau.

[1] Published in *Sugar*, Dec., 1925, p. 587.

[2] Bulletin No. 1389.

size of the container in which it was stored. The larger metal containers seemed to be slightly better for this purpose than the other commercial packages. Material stored in tightly stoppered glass bottles deteriorated slightly less than that stored in cans.

The loss in available chlorine was somewhat greater from powder stored in the hottest months than from that stored in the coldest months. The visible rays of light seemed to have a slight accelerating effect on the loss of available chlorine.

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**The Economy Coefficient of Phosphorescing Substances.** F. SCHMIEDER. (*Ann. d. Phys.*, No. 12, 1925.)—This coefficient is the ratio of the energy of the light emitted by the phosphorescing substance to the energy of the light that produces the effect. In all, six determinations were made. Three phosphorescent combinations were examined, CaBi, ZnCu, and CaCu. One band in the light emitted by each of these was used and for each band two different wave-lengths were employed for excitation. The largest coefficient found was .97 and the smallest .64, but a very simple relation underlies these diverse ratios. In 1914 Lenard made a single determination of the coefficient and interpreted his result as meaning that one quantum of light in the exciting radiation caused the giving out of one quantum of the phosphorescent light. The magnitudes of these quanta are, however, not the same. Each is the product of Planck's constant by the frequency of the light of which it is a part, so that the shorter the wave-length, the larger is the quantum for that wave-length. In fact the magnitude of the quantum for any definite color of light is inversely proportional to the corresponding wave-length. Let us consider the emission of phosphorescent light of $515\mu\mu$ wave-length under the excitation of light $365\mu\mu$ in wave-length. The quantum of the former is $\frac{365}{515}$, or .71, as large as that of the incident light. The economy coefficient by experiment was found to be equal to .73. This result, and indeed the results in all six cases, shows that, as Lenard believed, one quantum of exciting light produces one quantum of phosphorescent light. The value of the coefficient seems to be independent of any relation of sensitiveness or of lack of sensitiveness held by the exciting light with respect to the band of emitted light. "Nowhere is there discovered any other influence of the exciting light upon the coefficient than that which is founded upon the size of its quantum." G. F. S.

## NOTES FROM THE U. S. BUREAU OF MINES.*

### PROPERTIES OF BIS-TRIMETHYLETHYLENE NITROSATE.

By C. A. Taylor and Wm. M. Rinkenbach.

In the course of investigations of the structure and properties of various explosives and explosive compounds with a view to obtaining definite data as to their value as an explosive, the writers found it necessary to prepare amylene nitrosate, and their observations have developed new facts concerning the structure and properties of this explosive.

Solid, bimolecular amylene nitrosate has been found to exist in two optically inactive crystal forms—namely, needle-like forms and pseudo-cubes—having different melting-points; these representing a new form of stereoisomerism. Transformation from one form to the other is brought about by the action of heat and solvents, and this action is reversible.

Both forms are relatively unstable, but the needle form has the lower melting-point and is the more unstable of the two. The needle crystals melted at 86 to 90.4° C., while the pseudo-cubes gave values of 93.2 to 98.5° C. Both forms decompose on melting with the evolution of red oxides of nitrogen.

Several possible structures were found, and the probability that one of these holds is indicated. On account of its low sensitivity, it is of little interest as an explosive. Further details are given in a paper being published in the *Journal of the American Chemical Society*.

### SOLUBILITY AND EFFECTS OF NATURAL GAS AND AIR IN CRUDE OILS.

By D. B. Dow and L. P. Calkin.

The study of oil production with reference to the amount of oil originally present in the oil-bearing sands, which has engaged the attention of petroleum engineers for many years, has shown that ordinary methods of production remove only part of the oil, and it is generally realized that when a field is abandoned more oil remains in the sand than has ever been removed. Early studies

* Contributed by the Director.

by the Bureau of Mines and other agencies have shown that usually the total production of a field depends more on the available gas present with the oil than on the available oil. When the gas in the sand is exhausted, oil ceases to flow into the well, although there may be enormous quantities unrecovered.

The Bureau of Mines, in investigating the efficiencies of various methods for increasing recoveries from oil wells, began in 1920 a study of the solubility of natural gas in crude oil, with a view to obtaining fundamental data on the effects with relation to movement of oil in an oil sand. In this work, which has been continuous since that date, fundamental data have been obtained on the effects of pressure and temperature on the amounts of natural gas and air capable of being held in solution in different crude and refined oils, and the effect on gravity, volume, and viscosity of the crudes. The most striking feature of the results is the effect on viscosity. The experiments show that under the conditions of test, with most of the crudes tested, the effect of dissolved air is to increase the viscosity of the crude, and the effect of dissolved natural gas is to decrease the viscosity. A report is being issued on the results of the work as Serial 2732 of the Bureau of Mines.

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## GASES FROM BLASTING IN HEAVY SULPHIDES.

**By E. D. Gardner, G. W. Jones, and J. D. Sullivan.**

FIELD tests were completed in the sampling and analysis of gases in stopes and headings of certain western metal mines where the ore is largely massive pyrite. In blasting in heavy sulphide ores, there have been some serious accidents from the gases produced in blasting. The bureau's tests showed that the gases from blasting in such ore may not only carry dangerous amounts of sulphur dioxide, as had been suspected, but also hydrogen sulphide, which is an intensely poisonous gas. Recommendations were made which, it is believed, will prevent the recurrence of accidents from this cause. The chief precaution is to provide ample ventilation, and to permit enough time to dilute thoroughly and sweep out the gases after each blast, before the men are permitted to return to work. Further details are given in Serial 2734.

## TRANSMISSION LOSSES OF NATURAL GAS.

**By E. L. Rawlins.**

The Bureau of Mines, in coöperation with the Natural Gas Association of America, is conducting an extensive survey of losses from leakage of natural gas in pipe-lines, with the object of determining amount of leakage, its causes, and methods of prevention. Tests have been completed on several systems, and the results show that large savings can be made by systematic leakage surveys on the part of the operators. For example, tests by the bureau engineers on one system equivalent to 22.3 miles of 3-inch pipe showed an annual loss of 95,266,000 cubic feet, valued at $25,714. Repairs made as a result of the bureau's tests and recommendations reduced the loss to 49,249,000 cubic feet, or $13,291, an annual saving of $12,423. On another line tested, equivalent to 73.3 miles, the loss was reduced from $63,768 to $21,941, which is a saving of $41,827. On a third line, equivalent to 113 miles of 3-inch pipe, the loss was reduced from $27,148 to $17,370, or a saving of $9778 annually. These three lines were selected as typical systems, one being of screwed pipe, the second of rubber-coupled pipe, and the third, of welded pipe. The total savings on the twenty-six lines so far tested by the bureau amount to 237,704,000 cubic feet yearly, or an annual saving of $64,208. For a ten-year period, this saving with interest at 7 per cent., compounded annually, would be approximately $1,172,740. These figures, on a few of the many gas lines in this country, indicate the magnitude of the problem. Intensive study of the problem is being continued as rapidly as tests can be conducted. A fuller description is presented in Serial 2737.

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**On the Propagation of X-ray Impulses.** A. Joffé and N. Dobronrawov. (*Zeit. f. Physik*, Vol. 34, Nos. 1 and 2.)—A cavity 8 mm. in diameter in a block of hard rubber is made to serve as an X-ray tube. The anticathode is a piece of aluminum foil .005 mm. thick, which at the same time closes an opening between the tube and the outside. The impulses of X-rays set up by the impact of the electrons upon the foil pass through it and reach the space between the plates of a Millikan condenser where a particle of bismuth floats. With proper temperature regulation this would stay for hours in the same spot without gaining or losing an electron. Upon the operation of the adjacent X-ray tube the particle was observed to lose an electron at intervals of from twenty to forty minutes. The impulses of X-rays followed one another regularly about 1/1000

second apart. The possibility that the electron gets and stores up the energy brought to it by the million impulses that issue from the time of the emission of one electron to that of the next is considered and rejected. The radius of the floating particle was from $1 \times 10^{-5}$ to $5 \times 10^{-5}$ cm. It was situated .2 mm. from the origin of the impulses. Thus the solid angle subtended by the particle viewed from the origin was $10^{-6}$ to $2 \times 10^{-5}$.

"The energy of an impulse is emitted within a solid angle of $10^{-5}$. Consequently the rest of space is free from any energy belonging to this impulse. The observations here described lead us, therefore, to maintain the corpuscular propagation of radiant energy." The authors look forward to using a Wilson cloud-chamber for a further test of their work, which was done in the Röntgen Institute in Leningrad. G. F. S.

**The Measurement of Magnetic Fields by the Use of Streams of Liquid Conveying an Electric Current.** G. SCHMALTZ. (*Zeit. f. Physik.*, Vol. 35, No. 1.)—As long ago as 1823 Sir Humphry Davy noticed that a magnetic field deflects a stream of liquid through which a current is passing. In 1879 Silvanus Thompson made a fresh study of this effect. The forces acting on the stream are gravity and the force due to the reaction between the field and the current. The latter is measured by the product of the field strength perpendicular to the axis of flow by the current strength. A particularly simple case arises when this product just compensates both in size and in direction for the weight of the moving liquid, so that the stream shows no curvature though it has a horizontal component. The compensation is effected by varying the strength of the electric current until all curvature disappears. When this is attained the form and position of the stream are not affected by varying its velocity. The stream may be observed through a microscope and the velocity changed by rhythmically pressing and releasing the rubber tube conveying the liquid to the orifice. If the stream is really straight, it continues straight in spite of the varying velocity.

A satisfactory arrangement for measuring magnetic fields consists of a stream of mercury impinging on a piece of platinum. The electric current flows between the reservoir of liquid and the platinum. The orifice, a strictly circular opening .1 cm. in diameter, in a capillary tube, discharges the mercury coming from the reservoir through a rubber tube. From orifice to platinum a distance of from 2 to 5 cm. suffices. The pressure head should be 2 to 4 cm. of the liquid, so that the speed of efflux is at least 60 cm. per second. The lines of the magnetic field to be measured should be placed so as to run horizontally at right angles to the stream. With 20 amperes in the stream the flow is rectilinear when the field is 52 gauss; with .02 ampere, compensation occurs with a field of 52,000 gauss. The claim is made that an accuracy of measurement exceeding .1 per cent. can be reached by this method. G. F. S.

# THE FRANKLIN INSTITUTE.

*(Proceedings of the Stated Meeting held Wednesday, February 17, 1926.)*

THE stated monthly meeting of The Franklin Institute was called to order at eight-fifteen P.M. by President W. C. L. Eglin.

The President stated that the minutes of the last meeting had been printed in full in the February number of the JOURNAL of the Institute and that unless there were objection, they would be approved as printed.

There being no objection offered, the minutes were declared approved as printed.

The Secretary reported from the Board of Managers that since the last meeting, nineteen new members had been elected to the Institute. Of this number, five were Non-resident, the remainder Resident members.

The Secretary read the lists of members who were appointed by the President to constitute the Library Committee, the Meetings Committee, and the Museum Committee of the Institute for the year 1926:

| *Library Committee.* | *Meetings Committee.* | *Museum Committee.* |
|---|---|---|
| Fulweiler, W. H., Chairman | Howard McClenahan, Chairman | Bilgram, Hugo, Chairman |
| Bates, C. W. | Barnes, J. | Benzon, G. H., Jr. |
| Bonine, C. E. | Chesterman, F. J. | Church, A. L. |
| Creighton, H. J. M. | Crampton, G. S. | Clark, T. F. |
| Hall, C. A. | Hoadley, G. A. | Day, C. |
| Hepburn, J. S. | Penrose, C. | Hoadley, G. A. |
| Hoadley, G. A. | Rosengarten, G. D. | Houston, J. J. L. |
| Levy, L. F. | Sellers, C., III | Leffmann, H. |
| Price, M. M. | Swann, W. F. G. | Penrose, C. |
| Stradling, G. F. | Wetherill, W. C. | Quimby, H. H. |

By request, the Secretary called to the attention of the meeting a circular issued by the Philadelphia Commission concerning a proposed award of $5000, and stated that additional copies of this circular could be procured from the Philadelphia Commission, 1320 Packard Building, Philadelphia, Penna.

There being no further business, the President introduced the speaker of the evening, Major Theodore Lyman, Professor of Physics in Harvard University and Director of the Jefferson Laboratory of that University. Major Lyman spoke on "Radiations" and particularly upon the developments and discoveries made during the last four years in the extreme ultra-violet. The lecture was followed by a discussion of some phases of the talk by Prof. Karl T. Compton, of Princeton University.

The President adjourned the meeting at nine-eight P.M., with an expression of sincere appreciation to Professor Lyman for his interesting and instructive lecture.

HOWARD MCCLENAHAN, *Secretary.*

## COMMITTEE ON THE SCIENCE AND THE ARTS.

*(Abstract of Proceedings of Stated Meeting held Wednesday, February 3, 1926.)*

HALL OF THE COMMITTEE,
PHILADELPHIA, February 3, 1926.

MR. HAROLD CALVERT *in the Chair.*

THE Chairman announced the re-election by the Board of Managers of eighteen members of the Committee to serve for three years and the following new members to serve for three years:

Mr. N. W. Akimoff.
Mr. William L. Brown, 3rd.

To serve for two years:

Mr. William L. Austin.

The Special Committee on Nomination of a Chairman for the ensuing year reported as its choice Mr. Clarence A. Hall. Mr. Hall was unanimously elected and took the Chair.

The following reports were presented for final action:

No. 2841: Linerite.

Linerite is the trade name of a resilient material, of india rubber composition, made for lining the cylinders of ball and rod mills that are used in grinding and pulverizing ores, cements and other materials, and is designed to lessen operating expense by reducing wear and increasing capacity.

These pulverizers or ball mills are cylinders rotated on hollow trunnions, one end being higher than the other. The material to be pulverized is introduced into the upper end through the trunnion, and with it are introduced the balls by which the grinding is done. These balls are made of cast steel, and in a mill seven feet in diameter about eight tons of balls are used. As the mill is rotated these balls are carried up the rising side with the ores, and on falling strike the ores and pulverize them either between the lining and the balls or between the balls themselves. Linings usually consist of either chrome or manganese steel from two to three inches in thickness.

Both the balls and the lining are worn out in the process and need to be replaced. New balls can be introduced through the trunnions as needed without stopping the mill, but in order to replace a worn-out lining the mill must be stopped, emptied entirely, the old lining taken out and a new one put in. In addition to the wearing of the lining in a steel-lined mill there is a wearing of the shell of the mill itself on account of the grinding action of small particles of the ores working their way between the lining and the shell.

In order to overcome disadvantages a rubber lining has been devised for which U. S. Patent No. 1,470,597 was granted to Mr. James J. Denny and Mr. Rolla B. Watson, of Cobalt, Province of Ontario, Canada.

The objects of the invention are stated in the patent as follows: "To minimize the wear in pulverizing or granulating machines such as used in the maximum service of the machine, and further to provide an improved liner for the machine which will be materially lighter than the form of liners at present in use and will, therefore, absorb less power."

"In consideration of the successful application of a rubber lining to rotary

grinding mills, the Committee recommends the award of the Edward Longstreth Medal to Mr. James J. Denny, of Cobalt, Canada."

No. 2845 and No. 2846 } The Franklin Medal.

The following reports were presented for first reading:

No. 2842: Work of Dr. Charles S. Hastings.

No. 2849 and No. 2850 } Literature.

GEO. A. HOADLEY,
*Secretary to Committee.*

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## BARTOL RESEARCH FOUNDATION.

### FOUNDATION LECTURES BY DR. E. O. HULBURT.

Naval Research Laboratory.

A SERIES of three lectures will be delivered on March ninth, March twelfth, and March seventeenth, respectively, by Dr. E. O. Hulburt, of the Naval Research Laboratory, Washington, D. C., in the Lecture Hall of The Franklin Institute, at four P.M.

These lectures will be open to the members of the Institute and to those especially invited to attend. Requests for cards of admission should be addressed to—The Secretary, The Franklin Institute, 15 South Seventh Street, Philadelphia, Penna.

Synopses of the lectures are given herewith.

Tuesday, March 9th. "The Kennelly-Heaviside Layer and Radio Wave Propagation."

A quantitative theory, giving a clear picture of the manner of the passage of radio waves over the surface of the earth, has resulted from the recognition and measurement of the "skip distance" for radio waves below 40 metres in length. The electrons of the upper atmosphere, known as the Kennelly-Heaviside Layer, activated by the earth's magnetic field, play a crucial rôle. The shorter waves are propagated long distances by refraction in the layer and reflection at the ground, not by earth-bound waves, reaching heights of about 100 miles. At this height there are $10^5$ electrons per c.c. The theory explains many complex phenomena of fading, directional variation, and reception with vertical and horizontal Hertz antennæ. It predicts that waves below 14 metres cannot be used efficiently for long-distance terrestrial communication, but offer a possibility of interplanetary communication.

Friday, March 12th. "Hydrogen Spectrum Lines in the Stars and in the Laboratory."

The Balmer series of hydrogen, the simplest series of the simplest of terrestrial elements, finds its most striking development in the spectra of the stars and in the "flash spectrum" of the sun. The lines themselves vary greatly in the different spectra, being bright, dark, narrow, broad, singly, doubly, triply and asymmetrically reversed, etc. The investigations of these lines, although only partly accomplished with the relatively weak apparatus of the laboratory, com-

bined with modern theories of Stark effect and ionization, contribute definite knowledge of the conditions in the stellar atmospheres. In some stars are indicated large expanses of glowing hydrogen at a low pressure suffused with many electrons. In other stars more complex conditions of pressure, etc., evidently exist. The behavior of certain stellar hydrogen lines remains unexplained.

Wednesday, March 17th. "The Pressure of Light on Electrons."

Expressions for the pressure of a beam of electromagnetic radiation on a cloud of electrons are derived on a classical and a quantum theory. The classical calculation makes use of the usual formulæ of radiation pressure. The quantum calculation is statistical and involves the Compton Effect and the Correspondence Principle. For wave-lengths below 0.01 Å. the quantum expression predicts less pressure than the classical one. Numerical estimates indicate that the pressure is small unless there are many electrons or intense radiation, as may exist in stellar atmospheres, and offer an explanation of the negative results of H. A. Wilson, Langmuir, and others, and of the positive results of the fish track experiments of C. T. R. Wilson and of Bothe.

## MEMBERSHIP NOTES.

### ELECTIONS TO MEMBERSHIP.

*(Stated Meeting, Board of Managers, February 10, 1926.)*

#### RESIDENT MEMBERS.

MR. MORRIS L. CLOTHIER, President, Strawbridge and Clothier, Philadelphia, Penna.

MR. DONALD C. A. BUTTS, Research Physicist and Chemist, 4402 Walnut Street, Philadelphia, Penna.

MR. GUY HARTWELL ELMORE, Consulting Engineer, 1505 Race Street, Philadelphia, Penna. For Mailing: 201 Elm Avenue, Swarthmore, Penna.

MR. ANDREW A. KUCHER, Consulting Engineer, Westinghouse E. and M. Company, South Philadelphia Works, Philadelphia, Penna. For Mailing: 812 Glen Terrace, Chester, Penna.

MR. NEWTON LAMB, Chemist, Penn Process Company, Inc., Mill and Church Roads, Elkins Park, Penna. For Mailing: 349 Harrison Avenue, Elkins Park, Penna.

MR. SOLOMON M. SWAAB, Civil Engineer, 210 City Hall, Philadelphia, Penna. For Mailing: 1629 Diamond Street, Philadelphia, Penna.

DR. ROBERT H. WILHELM, Chemist, 509 South Tenth Street, Philadelphia, Penna. For Mailing: 4016 Spruce Street, Philadelphia, Penna.

MR. SYDNEY L. WRIGHT, JR., Chemist, Pennsylvaina Hospital, Eighth and Spruce Streets, Philadelphia, Penna. For Mailing: Greene Street and School House Lane, Germantown, Penna.

#### NON-RESIDENT MEMBERS.

DR. OLIVER E. BUCKLEY, Electrical Engineer, 463 West Street, New York City, N. Y.

MR. HENRY M. CANBY, Wholesale Lumberer, 600 Equitable Building, Wilmington, Del.

DR. CHARLES H. KUNSMAN, Physicist, Fixed Nitrogen Research Laboratory, United States Department of Agriculture, Friendship P. O., Washington, D. C.

MR. FRANK AUSTIN LIDBURY, President, Oldbury Electro-Chemical Company, Post Office Box 619, Niagara Falls, N. Y.

MR. LUTHER M. R. WILLIS, Lawyer, 213 St. Paul Place, Baltimore, Md.

CONTRIBUTING MEMBERSHIP.

E. G. Budd Manufacturing Company:

EDWARD SHUMWAY, Merion, Penna.

E. F. BATES, 248 Sheldon Street, Philadelphia, Penna.

CHESTER SCULL, JR., 2745 North Twenty-third Street, Philadelphia, Penna.

THEODORE KUEHN, 3232 North Twenty-sixth Street, Philadelphia, Penna.

DAVID NIELSON, 350 Johnson Street, Bristol, Penna.

FRANK D. ROGERS, 1702 West Erie Avenue, Philadelphia, Penna.

CHANGES OF ADDRESS.

MR. GEORGE BREED, 2127 St. James Place, Philadelphia, Penna.

MR. E. G. EBERLE, 10 West Chase Street, Baltimore, Md.

MR. MAURICE FELS, 4323 Spruce Street, Philadelphia, Penna.

MISS ANN W. FRY, 6433 Cherokee Street, Germantown, Philadelphia, Penna.

DR. CHARLES C. HARRISON, 1520 Locust Street, Philadelphia, Penna.

MR. BENJAMIN WILEY SANDS, 342 Fifth Street, S. E., Washington, D. C.

MR. R. P. C. SANDERSON, Moylan, Penna.

MR. ROYAL B. STEVENS, Bell Telephone Company, 261 North Broad Street, Philadelphia, Penna.

MR. HOWARD STOERTZ, 430 West Durham Street, Mt. Airy, Philadelphia, Penna.

MR. FRANCIS J. STOKES, Olney, Philadelphia, Penna.

MR. J. A. L. WADDELL, 150 Broadway, New York City, N. Y.

MR. JOHN S. WILSON, 429 West Pratt Street, Baltimore, Md.

## NECROLOGY.

**Mr. Howard B. French,** Philadelphia, Penna.

**Mr. Joseph B. McCall,** Philadelphia, Penna.

**Mr. Thomas H. Marshall,** Philadelphia, Penna.

**Mrs. Augene P. Rogers,** Philadelphia, Penna.

## LIBRARY NOTES.

RECENT ADDITIONS.

Allen's Commercial Organic Analysis. Fifth edition. Vol. iv. 1925.

American Annual of Photography, 1926. Vol. xl. 1925.

American Society of Heating and Ventilating Engineers. Transactions 1924–1925. Vols. xxx and xxxi. 1925.

BACK, E., and LANDÉ, A.—Zeemaneffekt und Multiplettstruktur der Spektrallinien. 1925.

BADGER, W. L.—Heat Transfer and Evaporation. 1926.

BLOCK, BERTHOLD.—Rübensirup. 1920.

BORN, MAX.—Vorlesungen über Atommechanik. Erster Band. 1925.

BRAGG, SIR W. H. and W. L.—X-rays and Crystal Structure. Fifth edition. 1925.

Brassey's Naval and Shipping Annual. 1926.

BROGLIE, MAURICE DE.—X-rays. Translated by J. R. Clarke. No date.

Bulletin Year Book and Almanac, 1926.

CLAYDEN, ARTHUR W.—Cloud Studies. Second edition. 1925.

COX, HENRY EDWARD.—The Chemical Analysis of Foods. 1926.

ELSNER, FRITZ.—Die Praxis des Chemikers. Ninth edition revised by W. Plücker. 1924.

FALOON, DALTON B.—Zinc Oxide: History, Manufacture and Properties as a Pigment. 1925.

FORD, LOUIS R.—Practical Marine Diesel Engineering. 1925.

GUNTHER, R. T.—Historic Instruments for the Advancement of Science. 1925.

HART, MORRIS D., and SMITH, W. WHATELY.—The Principles of Sound Signalling. 1925.

HOLMYARD, E. J.—Chemistry to the Time of Dalton. 1925.

LILLEY, ERNEST RAYMOND.—The Oil Industry. 1925.

MACARDLE, DONALD W.—The Use of Solvents in Synthetic Organic Chemistry. 1925.

MELLOR, J. W.—A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. vi. 1925.

MÜNSTER, C., and RADESTOCK, W., editors.—Zuckersteuergesetz, Süssstoffgesetz, Kakaozollvergütung. 1925.

MURRAY, W. S.—Superpower. 1925.

PARTINGTON, J. R.—The Alkali Industry. Second edition. 1925.

Photograms of the Year 1925.

SIEGBAHN, MANNE.—Spektroskopie der Röntgenstrahlen. 1924.

TRUMPER, MAX.—Memoranda of Toxicology. With Introduction and Addenda by Henry Leffmann. 1925.

U. S. Department of Commerce. Commerce Year Book for 1922, 1923 and 1924. Three volumes. 1923–1925.

WARNES, ARTHUR R.—Coal Tar Distillation and Working Up of Tar Products. Third edition. 1924.

Wasserkraft Jahrbuch 1924.

WEBER, GUSTAVUS A.—The Bureau of Standards: Its History, Activities and Organization. 1925.

WILSON, SAMUEL P.—Pyroxylin Enamels and Lacquers. 1925.

World Almanac and Book of Facts for 1926.

## BOOK REVIEWS.

THE CHEMICAL ANALYSIS OF FOODS. By Henry Edward Cox, M.Sc., Ph.D., F.I.C. vii–323 pages, illustrated, small 8vo. Philadelphia, P. Blakiston's Son and Company, 1926. Price, $5.

The subject of food analysis has become so extensive of late years that a large volume is required to cover the general and special procedures. The author of this book has succeeded in comprising a large amount of information and expressing it in clear form, but being fully conscious of the limitations

of the volume, the elements only of the subject have been presented in a manner suitable to chemists who have had no special experience in the field. Only methods which have been well tested and found trustworthy are given as a rule, but in some cases provisional processes have been described as no wholly satisfactory ones are available. The point of view is rather that of the public health official and of the (British) Sale of Food and Drugs Acts, than of the workers in any particular branch of food industry. A competent knowledge of general analytical chemistry and familiarity with the standard instruments of the laboratory are assumed. Microscopy of foods has not been much developed. The author feels that such phases should be left to special works. There are a few drawings of microscopic fields, but, as a matter of fact, such, even when most carefully done, are but poor substitutes for actual experience. The study of the microscopy of food as with all other fields of application of the microscope should be with instruments and specimens properly illustrative.

The work is notably from the British standpoint. There are, of course, many points of contact in food analysis in the different countries, but each nation has its specific problems. American work is not strongly featured, indeed in some respects it seems to be definitely ignored.

HENRY LEFFMANN.

THE USE OF SOLVENTS IN SYNTHETIC ORGANIC CHEMISTRY. By Donald W. MacArdle, B.S., Boston University. vii–217 pages, 8vo. New York, D. Van Nostrand Company, 1925. Price, $3.50.

This is a very interesting and valuable work. The nature of solution has been very extensively discussed in physical chemistry, but this work deals with the practical features of the use and applications of solvents. It is planned as the initiative of a series of essays on the operative technique of synthetic organic chemistry similar to the German works of Lassar-Cohn and Weyl. It appears that it was first intended to simply translate these books, but it was found that an immense amount of revision was needed and it was decided to build up from the base. Necessarily the book is a compilation, but it is none the less welcome and its production commendable. The bibliography, which is naturally very extensive, is covered by a concentration of the references in the back of the book, each reference being by a serial number. This method has considerable advantage. The references are given very satisfactorily, year and volume when available being included. In many cases the abstract in C. A. or other abstract journal is given. The fact that slightly over nine hundred distinct references are given shows how searching has been the work of compilation.

The data include methods for the preparation of solvents in pure form, among which much attention is given to the preparation of absolute alcohol. In the chapter on the promotion of crystallization many interesting and useful facts are set forth. The purpose of the chapter is to furnish information as to how crystals may be secured and not produce specially fine or typical forms. Another phase of the subject which has no direct concern with the scope of this book is the obtaining of large perfect crystals, such as were desired during the war for application in piezo-electrical tests. Very ingenious and useful

work was done in American laboratories in this line, crystals of sodium potassium tartrate several inches in size and perfect in form being obtained.

Though primarily intended, as stated in the title, for workers in synthetic organic chemistry, the book will be of much use to research workers in other fields and also to those engaged in general analysis.

HENRY LEFFMANN.

POPULAR RESEARCH NARRATIVES. Vol. 2. Collected by the Engineering Foundation. viii–174 pages, 12mo. Baltimore, The Williams and Wilkins Company, 1926.

This is a series of fifty short papers relating interesting and important work in invention and discovery in many departments of science, pure and applied. Being especially intended for the general reader, it employs, as far as possible, non-technical language. As it has such a wide range of subjects it affords to the professional scientist much valuable information, because no one, however versatile, can be fully acquainted with all the topics. Among the papers is one on the improvement in platinum mining in the Urals, brought about by careful study and ingenious suggestions. Hardly any information is more welcome to the chemist than news that the supply of platinum may be increased. It would be a great boon if the element could be discovered in such quantity as to bring its price below that of gold, in which case, Mrs. Gosch Whatta Pyle would cease appropriating it for her jewelry and chemists would be able to get the practically irreplaceable material at reasonable cost. A good deal of history is incorporated in the contributions, which fact adds to the interest and value. The series is intended to help the movement now going on in the United States to bring to the people thereof a full sense of the importance of research in the lines of pure and applied science.

HENRY LEFFMANN.

MEMORANDA OF TOXICOLOGY. By Max Trumper, B.S., A.M. Pocket size, xii–230 pages. Philadelphia, P. Blakiston's Sons and Company, 1925. Price, $1.50.

This book presents in very convenient form the data concerning the nature, effects, treatment and detection of the poisons that are likely to be encountered in general practice. Though announced as partly based on Tanner's "Memoranda on Poisons," Mr. Trumper has added a large amount of information, especially drawing from American experience. His residence for several years in Jefferson Hospital and his courses of lectures on toxicology in the College, have enabled him to obtain knowledge of the most recent methods of treatment of poisonings. There has, indeed, been considerable advance made in this line, and the familiar "List of antidotes" in students' manuals and *vade mecum* books is no longer a safe guide. Specially worthy of note are the data concerning the dangers from poisoning among children from the unrestricted sale of caustic alkalies for household use, the large experience of Dr. Chevalier Jackson and his associate, Doctor Clerf, in Jefferson Hospital, being comprehensively presented. The new gasolin addition, tetrethyl lead, is fully treated. Addenda giving information on the subject of "poison rum," and a discussion as to "What is a poison?" add to the value of the work. The data

concerning the adulterants found in illicit liquors will be of much interest and value.

The text of the book is carefully and clearly written and the publisher has issued it in a convenient and attractive form. It is a book that will be very useful to the student and equally so to the practising physician and toxicologist.

HENRY LEFFMANN.

TABLES NUMÉRIQUES DES ÉQUATIONS DE LAGRANGE. Par Niels Nielsen, Professeur a l'Université de Copenhague, Membre de l'Academie Royale des Sciences. xviii–400 pages, 6 x 9 inches, paper. Copenhagen, Gyldendalske Boghandel; Paris, Gauthier-Villars, 1925.

The theory of numbers occupies a unique place in mathematical history. Unlike other branches which have advanced by gradual development, its early modern progress has been by spectacular contributions of individual genius. Until relatively recent times, advances in science in general were the result of this individual initiative and effort; systematic coöperation in research was unknown. It is true there are to-day no great establishments exclusively for mathematical research kindred to Foundations in special branches of science, but the freedom in publication of modern times has done much to bring about a quasi-coöperation among workers in widely separated areas. In the days of the early great leaders of modern mathematical thought, the names of Fermat, Euler, Lagrange and Gauss outstand. Fermat, who was the initiator of the modern school of number analysis, announced his theorems without demonstration, and to the genius of Euler fell an important share in supplying their rational derivation and disentangling difficulties of that refractory subject. Only one of Fermat's theorems has proved not true, but that one, it may be noted, Fermat presented with due reservation.

Euler in his algebra dealt very fully with the solution of indeterminate equations, applicable to number theorems and in the French edition of this work notable additions and amplifications of these devices were supplied by Lagrange. It was the fifth of these supplements, the present author states, that led Gauss to the development of the theory of quadratic forms, a theory which for a century dominated in researches on the equation of Lagrange:

$$n^2 - av^2 = (-1)^\omega .$$

Modern investigators are inclined to seek general laws by a prodigal application of the statistical method, and adequate tables of integers which satisfy the various forms which expressions assume in dealing with number theorems are obviously an invaluable aid. The present work is such a collection of the values of the $n$, $v$ and $\omega$ under the argument $a$ in the above formula and other related values in the same or in transformed formulas.

There is no text in the body of the work except the explanatory captions with each table. The only explanatory notes occur in the preface of thirteen pages which indeed contains a surprising amount of information in its small compass. There are eleven tables of which Table I and Table II of the above formula occupy 171 pages. The list is as follows: Table I—Bases $a = 2$ to 102. Table II—Certain bases greater than 102. III—Bases of the first kind. IV—

Simultaneous equations. V—Non-elemental bases of Tables I and II. VI—Prime numbers less than 5600 (with $a = 8n + 1, 3, 5$ and $7$; and some primes greater than 5600). VII—Certain sums of two squares. VIII—Bases of the second kind. IX—Non-elemental bases. X—Summary of certain sums of two squares. XI—Summary of products of two prime numbers.

The work is evidently intended for mathematical investigators rather than for those who utilize the results of mathematical research and do not primarily deal with the fundamentals of the subjects. The former type of users will find adequate information in the captions of the tables, but a larger class not so well qualified in the subject, yet deeply interested, would welcome a text on the subject. However, the tables occupy a fairly large volume and a text might require one as large or larger. The tables, which the author states have been duly checked, represent an immense amount of skilfully directed labor and constitute a valuable addition to the equipment of investigators in the theory of numbers. The press-work is of a high order of excellence.

LUCIEN E. PICOLET.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 225, The Air Forces on a Model of the Sperry Messenger Airplane without Propeller. By Max M. Munk and Walter S. Diehl. 12 pages, illustrations, quarto. Washington, Government Printing Office, 1925. Price, five cents.

This is a report on a scale-effect research which was made in the variable density wind-tunnel of the National Advisory Committee for Aeronautics at the request of the Army Air Service. A 1/10 scale model of the Sperry Messenger airplane with USA–5 wings was tested without a propeller at various Reynolds numbers up to the full scale value. Two series of tests were made: The first on the original model which was of the usual simplified construction, and the second on a modified model embodying a great amount of detail.

While the present report is of a preliminary nature, the work has progressed far enough to show that the scale effect is almost entirely confined to the drag. In the tests so far conducted, the drag at any given angle of attack within the normal flying range is found to vary as $\left(\frac{Vl}{\nu}\right)^n$. The exponent $n$ is constant for any one angle of attack, and ranges from $-0.045$ at large angles of attack to $-0.17$ at small angles.

It was also found that the model should be geometrically similar to the full-scale airplane if the test data are to be directly applicable to full scale. If the condition of geometric similarity be fulfilled, the data obtained at a full scale value of Reynolds number agree very closely with free-flight data. The variable density wind-tunnel therefore appears to be a very promising instrument for procuring test data free from scale effect. It is also admirably suited for studying the scale effect and obtaining information which is necessary in an interpretation of the results obtained in atmospheric wind-tunnels at low values of the Reynolds number.

Report No. 228, A Study of the Effect of a Diving Start on Airplane Speed. By Walter S. Diehl. 9 pages, illustrations, quarto. Washington, Government Printing Office, 1925. Price, five cents.

Equations for instantaneous velocity and distance flown are derived for an airplane which crosses the starting line of a speed course at a speed higher than that which can normally be maintained in horizontal flight. A specific case is assumed and calculations made for five initial velocities. Curves of velocity, average velocity, and distance flown are plotted against time for each case and analyzed. It is shown that the increase in average velocity due to a diving start may be very large for short-speed courses.

WASSERKRAFT-JAHRBUCH, 1924. Herausgeber: Oberbaudirektor K. Dantscher Ord. Professor, München, und Ingenieur Carl Reindl, München. 612 pages, illustrations, plates, 8vo. München, Richard Pflaum, 1924. Price, 24 marks.

The engineering professions have annuals and manuals on many subjects, but this is the first issue of a yearly publication devoted to water-power.

The three main divisions of the work comprise a review of the development and utilization of the water powers of Europe, the planning and construction of hydraulic power plants and the necessary machinery and apparatus for their equipment. An appendix contains tables and data especially useful to the hydraulic engineer. The work is well supplied with illustrations of many kinds, including plans for power installations, sections of turbines and other hydraulic machinery, tables of steam flow measurements, etc.

It is to be hoped that the editors will receive sufficient support in their undertaking to make the second issue international in scope.

## PUBLICATIONS RECEIVED.

*The Fundamental Concepts of Physics in the Light of Modern Discovery.* Three Lectures at the Carnegie Institute of Technology, Pittsburgh, January, 1925, by Paul R. Heyl, Ph.D. 112 pages, illustrations, 16mo. Baltimore, The Williams and Wilkins Company, 1926. Price, $2.

*The Use of Solvents in Synthetic Organic Chemistry,* by Donald W. MacArdle, B.S. 217 pages, 8vo. New York, D. Van Nostrand Company, 1925. Price, $3.50.

*Elementary Electrical Technology for Engineering Students,* by A. M. Parkinson. 179 pages, illustrations, 12mo. London and New York, Oxford University Press, 1925. Price, $2.

*Tables Numériques des Équations de Lagrange,* par Niels Nielsen, Professeur a l'Université de Copenhague. 400 pages, 8vo. Copenhagen, Gyldendalske Boghandel, 1925.

*Modern Magnetics,* by Felix Auerbach, Professor of Physics in the University of Jena. Translated by H. C. Booth, A.R.C.Sc. 306 pages, illustrations, 8vo. New York, E. P. Dutton and Company. Price, $6.

*The Physical Chemistry of Steel-making Processes.* A General Discussion Held by the Faraday Society and the Iron and Steel Institute. 296 pages, illustrations, plates, 8vo. London, Faraday Society, 1925. Price, 8 shillings 6 pence.

*Practical Photo-micrography,* by J. E. Barnard, F.R.S., and Frank V. Welch, F.R.M.S. Second edition. 316 pages, illustrations, plates, 8vo. New York, Longmans, Green and Company, 1925.

*National Advisory Committee for Aeronautics:* Technical Notes, No. 230,

The Spacing of Orifices for the Measurement of Pressure Distributions, by Max M. Munk. 48 pages, illustrations, quarto. Washington, Committee, 1926.

*Ontario Department of Mines:* Thirty-fourth Annual Report, being volume 34, parts II and III, 1925. 100 pages, illustrations, map, 8vo. Toronto, King's Printer, 1925.

*U. S. Bureau of Standards:* Circular No. 286, U. S. Government Master Specification for Asphalt-saturated Rag Felt for Flashings. 4 pages. No. 297, U. S. Government Specification of Plastic Fire-clay Refractories. 5 pages. Price, five cents per copy.

*U. S. Bureau of Mines:* Technical Paper 320, The Bureau of Mines Orsat Apparatus for Gas Analysis, by A. C. Fieldner, G. W. Jones, and W. F. Holbrook. 18 pages, illustrations, plate, 8vo. Washington, Government Printing Office, 1925. Price, five cents. Bulletin 197, Sampling and Examination of Mine Gases and Natural Gas. A revision of Bulletin 42, by George A. Burrell and Frank M. Seibert, revised by G. W. Jones. 108 pages, illustrations, plates, 8vo. Washington, Government Printing Office, 1926. Price, twenty-five cents.

*Canada Department of Mines, Mines Branch:* Investigations in Ceramics and Road Materials, 1924. 45 pages, 8vo. Ottawa, King's Printer, 1925.

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**The Light of the Night Sky.** LORD RAYLEIGH. (*Proc. Royal Soc.*, A 751.)—This is a continuation of observations already described and reported upon. On an arbitrary scale the smallest value for the total visible light of the sky was 3.4 and the largest 10.0. "It is of interest to remark that the highest value yet encountered—that of October 25, 1924—occurred on a night noted as 'not very clear.' Here again, we see how changeable transparency of the atmosphere fails to afford any sufficient explanation of the observed variations."

By the use of filters the light from the sky is divided into regions which are studied individually. One such region is that of the famous green line of wave-length 5577, which the author gives as 5578. He holds that this line "seen in the night sky in temperate latitudes is excited by a different agency from that which acts in polar regions." An attempt was made to correlate the intensity of this line in the night light with sun-spot areas, magnetic disturbances and barometric readings but without success. There seems to be connection between the season of the year and the intensity of sky light.

When J. H. Jeans visited the Mount Wilson Observatory in 1924 he took an instrument with him, with which observations were made. From these it appears that the auroral intensity in California is 2.2 times that in England.

"No regular variation of the auroral intensity can be detected in the course of the night. As soon as daylight has faded sufficiently to allow definite observations to be taken, the auroral intensity takes the value which prevails at midnight and until dawn."

Lord Rayleigh has organized a scheme for a world-wide study of the light of the sky and is sending out instruments for this purpose.

G. F. S.

# CURRENT TOPICS.

**Report on New Experiments with Super-conductors.** H. KAMERLINGH ONNES. (Communications, Phys. Lab., Leyden, Supplement No. 50.)—Up to the time of the experiments recorded here Kamerlingh Onnes had been able to use liquid helium only in a cryostat joined to the liquefying apparatus. When he got means of carrying the liquid to a cellar where there was little vibration and where the temperature was constant, it became possible to increase the sensitiveness of his observations on metals cooled to so low a temperature that practically all electrical resistance disappears.

Within a ring of lead was suspended a second ring of the same metal. The two rings are in the same plane and have the same centre. They are both converted into super-conductors by jacketing with liquid helium. A current is then induced in both by the variation of a magnetic field. Because the rings of lead have practically no resistance at the low temperature these currents persist for hours. A torsion head carrying the inner ring is turned until the latter rests in a plane at 30° to that of the fixed ring. This turning causes induced currents anew. After about twenty minutes a steady state is reached. The electrodynamic force between the currents in the two lead rings is counterbalanced by the torsion of the suspension. Any change in the strength of the currents would evidence itself by a shift in the position of the movable ring. For six hours mirror observations were carried on to detect any such shift. There were, it is true, very slight changes in position which were in such direction as to indicate an increase in the acting couple, but the author contents himself with the deduction that the currents remain constant within the limits of the precision of the experiments. This conclusion is so astounding that it is worth repeating. In lead cooled to the temperature of liquid helium an electric current once made to flow continues to flow for six hours without loss of strength, no electromotive force being in operation. The cautious statement is made that at most the change in current strength amounts in an hour to 1/20,000. "It is found then that the resistance of lead in the superconducting state cannot be above one-million-millionth of its value at 0° C., that is to say, by this experiment the residual resistance has shrunk to a value less than one-tenth of that which I previously assigned to it." Another set of experiments was made with a hollow lead ball replacing the inner ring. From these it appears that the sheet of currents on the sphere does not shift its position with the passage of time.

At the First Solvay Conference, Langevin made the suggestion that super-conducting lead is in a phase different from that of ordinary lead. Just before the Fourth Conference, at which this paper

was presented, Keesom, working in the Leyden cryogenic laboratory, applied the X-rays to this problem and found that the crystalline structure of lead at the temperature of liquid helium is the same as that of the metal at liquid hydrogen temperature, which is that at room temperature.

Indium was definitely found to become a super-conductor at 3.41° Abs. Gold, cadmium and gallium approach closely to this state, while sodium, potassium, aluminum and germanium do not approximate to it. G. F. S.

**Some Further Experiments on the Gyromagnetic Effect.** J. W. FISHER. (*Proc. Royal Soc.*, A 749.)—By rotating rods of magnetic materials Barnett has succeeded in developing and measuring magnetic fields with lines of force parallel to the axis of rotation. The magnetic particles, whatever they may be, set their axes of rotation in the same direction as the axis about which the rod as a whole rotates, just as a top with axis free to set itself in any position will adjust itself so that its axis is vertical if it be swung by hand in a horizontal plane, and will turn upside down on the reversal of the rotation. In the present paper is recounted a search for a similar magnetic field resulting from rotation not of the magnetic mass as a whole but of the separate particles composing it. A rotating magnetic field was applied to a magnetic substance, whose individual particles should, perhaps, themselves rotate in unison with the field and set their axes parallel to the axis of the field.

Eddy currents had to be avoided lest they keep the magnetizing field from penetrating the material under examination. A low electric conductivity was therefore necessary. This led to the choice of magnetite as a suitable magnetic substance. It was powdered and contained after compression in glass tubes. The rotating field came from the superposition of two linear harmonic fields at right angles to each other, and with a phase difference of 90°. The frequency of the field was about 53,000 per second.

It was calculated that an effect manifesting itself by a deflection of 690 mm. should be obtained, but not as much as a single mm. of deflection was noted. "No evidence of an effect of this kind was found, even for rotating fields of over 100 gauss." It may be, the author suggests, that the magnetic particles do not rotate with the field. In the Barnett experiment they are mechanically constrained to rotate. G. F. S.

**Diffraction by Line Screens.** L. R. WILBERFORCE. (*Phil. Mag.*, Nov., 1925.)—The author, professor of physics in the University of Liverpool, had a desire to put into the hands of his students of optics some kind of coarse diffraction grating in which the rulings could be examined with a microscope of low power. He obtained and tested one component of a line screen used in process photography. It consisted of a glass plate having 133 lines to the inch, the alternate opaque and transparent parts being of about equal

breadth. When this grating was mounted on a spectroscope it gave with sodium light a long series of spectra on both sides of the centre. Moreover the intensity of the spectra of high orders fell off very slowly and, in addition, the spectra of odd orders and those of even orders were of the same intensity. On examination the grooves which were filled with an opaque black pigment were found to possess remarkably sharp edges. "A result of such accuracy and uniformity must have been produced by some kind of mechanical ruling, together with subsequent etching, and it is clear that if the original plane surfaces of the glass between the opaque portions remained unaffected by these processes, the behavior of the grating must accord with elementary theory, and the spectra of even order should be absent or faint." It is suggested that in the preparation of these gratings the edges are in some way rounded off so as to cause a favoring of the even spectra. This supposition was confirmed in two ways. Cedar-wood oil of the same refractive index as plate glass was spread over the grooved side of the grating and upon it was placed a piece of glass whose outer surface was known to be plane, "so that wherever owing to want of perfect planeness some glass was absent, an equivalent thickness of cedar-wood oil would take its place." This combination used as a grating gave very faint even order spectra. Furthermore a contact photographic print of the line screen was tried as a diffraction grating and gave faint even order spectra.

"Subsequently I received an introduction to Messrs. Max Levy and Company, of Philadelphia, U. S. A., the manufacturers of these line screens, who treated me with great courtesy and presented me with specimens of ruled surfaces going up to 600 lines to the inch. Even these more closely-ruled gratings were remarkable not only for the accuracy of their spacing, but, what must be far more difficult to secure, for the sharpness of the edges of the lines, and for the uniformity of the ratio of the width of the transparent and opaque portions. I tested a number of them, alternately dry and mounted in cedar-wood oil, and the contact prints obtained from them, with results similar in character to those already described." With one of these gratings having 600 lines to the inch all the spectra up to the thirteenth could be seen. The intensity gradually diminished with increasing order.

This type of grating may thus serve a twofold purpose in the instruction of students. "If used dry, they may show an abnormally long series of spectra, and so give angles of diffraction large enough for fairly accurate measurements and if mounted in cedar-wood oil, they will behave like the ideal grating of elementary theory."

G. F. S.

**On Atmospheric Radio-activity and Indian Weather.** D. B. DEODHAR, University of Lucknow. (*Proc. Royal Soc.*, A 750.)—For two hours at a time a long, bare copper wire, stretched horizontally four feet above the ground in the open air and insulated by

glass rods, was kept at a negative potential of 3000 volts. It was then quickly wound up. Three minutes after it had been in the air it was put into the ionizing chamber of an electrometer whose rate of discharge was observed. One experiment a day was performed for the eight months from October to May. No difference in the effect was found by changing the voltage of the exposed wire from 1500 to 5000. The unit of activity of the atmosphere was that present when one metre of the wire discharged the electrometer one volt per hour. In such units the average monthly activity rose from 301 in October to a maximum of 550 in January, from which it descended to 250 in May. "On the whole, the activity in Lucknow is far greater than that observed by Simpson and Gockel in Europe." From a comparison of activity with the height of the barometer it is manifest that in India an increase of activity is generally accompanied by a fall of the barometer and *vice versa*. This is comprehensible on the view that the radio-active content of the atmosphere is due to the escape of active material from the soil. A reduction of the air pressure would facilitate this motion. It is, however, clear that at least a part of the radio-active effect depends on something coming from above, for "cloudy weather always shows small radio-activity, while clear weather is attended with higher values." The denser cumulus clouds reduce the activity more than cirrus clouds. Such observations are of interest in connection with Millikan's penetrating radiation.

G. F. S.

**Centenary of the American Journal of Pharmacy.**—In December, 1925, the *American Journal of Pharmacy* celebrated the one-hundredth anniversary of the publication of its first number in December, 1825. During the century of its existence, the journal has been published by the Philadelphia College of Pharmacy and Science for the advancement of pharmacy and the allied sciences, and the promotion of correlated education and research. It is the oldest pharmaceutical periodical published in the English language, and was for many years the only pharmaceutical journal in the United States. Its editors and the contributors to its pages have been eminent in pharmacy and the allied sciences. The centenary number contains a series of papers which summarize the advances in the arts and sciences, at home and abroad, during the past century. J. S. H.

**A New Quantitative Reagent.**—Citarin, the sodium salt of a complex derivative of citric acid, was introduced in 1901 by the Elberfeld Company as a therapeutic agent. In 1917, Vanino reported in the *Kolloid-Zeitsch.* (1917, **20**, 122) its use in colloid chemistry. Recently Vanino and Guyot have studied its application as a reagent for the determination of reducible metals. Their results, which as yet have been found satisfactory only with silver and gold, are reported in the *Ber. d. deut. Pharm. Gesell.* (1926, **36**, 98). When mixed with water, the salt undergoes hydrolysis with separation of formaldehyde and it was, therefore, inferred that reducible metals

would be set free. Decinormal silver nitrate was mixed with citarin solution and sodium hydroxide of similar strength, heated for thirty minutes on the water-bath and allowed to stand overnight. The precipitate was collected on a suitable filter, washed and dried (at from 110° to 120°). A similar method was applied to gold chloride solution. The test analyses submitted show very satisfactory data. Experiments with bismuth have so far not yielded useful results.

H. L.

**A New Stroboscopic Device with Strong Illumination.** L. and A. SEGUIN. (*Comptes Rendus*, Oct. 26, 1925.)—As long ago as 1873 Crova knew the use of a Geissler tube for the production of intermittent illumination at controlled intervals. With either a vibrating or a rotating interrupter, the arc formed by breaking the current limited the strength of the current in the primary, and consequently in the secondary coil also, so that the available current through the tube produced but feeble flashes of light. To avoid this hampering dependence of the intensity of light upon the current capacity of the interrupter, in the new apparatus the illumination comes from the discharge of a strong battery of condensers through a neon tube. This discharge cannot pass by its own voltage but must wait to be set off by an induced current due to the interruption of a current by the timing device. The intensity of the momentary illumination can, therefore, be made as great as is desired. It can in addition be caused to be practically instantaneous. In one case two marks, one mm. apart, could be clearly seen on a disc, illuminated by this device, even when it was rotating so that its periphery had a speed of 100 mm. per sec. The strong intensity of the flashes of light produced in the tube is of value in studying the motion and vibration of large and somewhat inaccessible machinery. G. F. S.

**The Thirteen-month Calendar.** (U. S. Department of Agriculture, Clip Sheet, No. 397, Feb. 1, 1926.)—Fresh stimulus has recently been given to the reform of the calendar by the action of the committee of inquiry of the League of Nations in calling representatives of the Roman, Greek, and other orthodox churches of the East, the Anglican Church of Great Britain, and about 100 Protestant churches to discuss the advisability of making Easter a fixed instead of a movable date, dependent on the full moon. The first or second Sunday in April has been suggested.

Further sessions of the committee of inquiry are to be held soon to make definite recommendations to the League of Nations regarding plans for calendar reform. Enthusiastic support has been given in many quarters to the plan that would divide the year into thirteen twenty-eight-day months, with an extra day at the end of the last week in December. Every four years a leap-year day would be inserted at the end of June. The change, it is said, could be made easily on January 1, 1928, as that will be Sunday.

Prof. C. F. Marvin, Chief of the U. S. Weather Bureau, indorses

the thirteen-month year because it would greatly simplify meteorological and other scientific records. He points out also that there are innumerable advantages to economic, agricultural, civic, educational, and business interests in having all months and quarters exactly alike, and the numbered days of each month always falling on the same day of the week. Many difficulties now existing in compiling accurate comparative statistics, in accounting, banking, or computing interest would be done away with.

An interesting fact in connection with the proposed calendar is that it harmonizes in many respects with the plan of the old calendar used by the Israelites.

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